FINAL GEOCHEMICAL REPORT ON ISSUES 3 AND 5

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REMEDIAL INVESTIGATION AND FEASIBILITY STUDY FEED MATERIAL PRODUCTION CENTER FERNALD, OHIO

Final Geochemical Report on Issues 3 and 5

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1.0 INTRODUCTION

1.1 BACKGROUND

A Work Plan for the sitewide Remedial Investigation and Feasibility Study (RI/FS) at the U.S. Department of Energy's (DOE's) Feed Materials Production Center (FMPC) in Fernald, Ohio was developed to evaluate potential uranium sources to the underlying aquifers and provide geochemical parameters for a three-dimensional model of groundwater flow and radionuclide transport. Recognizing the need for site-specific modeling data on the physiochemical processes that could affect radionuclide migration and attenuation, a geochemical testing program was included in the RI/FS Work Plan as part of the Subsurface Soils Sampling Plan. The geochemical program included analytical testing for total uranium, differential leaching of uranium, total cation exchange capacity, total organic carbon, leachable iron and manganese, and grain size on about 40 subsurface solid samples from three stratigraphic horizons below the FMPC. The purpose of the geochemical testing program was to quantify chemical parameters on aquifer solids which would enhance the evaluation of radionuclide migration and attenuation.

Subsequent to the submission of the original RI/FS Work Plan, a reconsideration of the geochemical data needs indicated a deficiency in some of the proposed analytical work. For groundwater samples, a field determination of dissolved oxygen and alkalinity, and laboratory analysis of calcium, potassium and phosphate, were considered critical additions to the program to satisfy the data needs for the geochemical modeling effort. For aquifer-solid samples, the leachates produced from the leachable iron and manganese test were split, and one split of each sample was retained for total fluorimetric uranium analysis. Each of these additional analytical procedures were eventually integrated into the geochemical testing program.

Because the groundwater-flow and solute-transport model will simulate only the sand and gravel aquifer underlying the FMPC and surrounding region, contamination reaching the aquifer as a result of vertical migration through the overlying till is dealt with as a source term to the model. That is, any past, present, or future uranium release from the till will be input to the model as a known quantity from each principal source. The role of the geochemical program was expanded to account for this model design and served as the focal point to evaluate the source terms for the model.

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1.2 ISSUES OF THE GEOCHEMICAL PROGRAM

The geochemical program conducted in support of the RI/FS is designed to:

- Evaluate past, current and future releases of uranium from several primary sources to the underlying aquifer
- Develop representative values for geochemical parameters that will be used to model solute transport in the groundwater.

In order to provide the most substantive results in a cost-effective manner, the technical approach to satisfy these objectives was developed around five key, site-specific issues. These five issues are:

- Does soil contamination from air deposition represent a source of uranium to groundwater
- Do soluble uranium spills represent a past, continuing or future source of uranium to groundwater
- Does Paddy's Run and/or the storm-water-outfall ditch represent a past, continuing or future source of uranium to groundwater
- Do the waste pits represent a past, continuing or future source of uranium to the underlying aquifers
- Geochemical parameters for radionuclide transport and attenuation in the sand and gravel aquifer must be estimated for use in the solute transport model.

The first four issues focus on field and laboratory data to estimate the amount of uranium available from potential sources, while the fifth issue additionally utilizes geochemical modeling and published literature to quantify a uranium distribution coefficient (K_d) for the aquifer. The uranium distribution coefficient is defined as the concentration of sorbed uranium per kg of aquifer solid divided by the concentration of uranium per liter of ground water [$K_d = \frac{mg}{kg}$]. This interim report will address issues three and five of the RI/FS Geochemical Program.

1.3 ISSUE THREE: PADDY'S RUN AND THE STORM-WATER-OUTFALL DITCH

1.3.1 Purpose and Scope

The purpose of issue three is to establish whether uranium-bearing surface water has infiltrated and/or continues to infiltrate vertically downward through the bottom of Paddy's Run and the storm-water-outfall ditch. Additionally, the disposition of this uranium prior to reaching the

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underlying sand and gravel aquifer needs to be established. To address this issue, subsurface soils and surface waters from Paddy's Run and the storm-water-outfall ditch (Fig. 1) have been sampled and analyzed to evaluate the retention capability of the soils and the degree of infiltration of uranium-bearing surface water to the underlying aquifer. Surface-water samples were analyzed for chemical parameters and the analytical data used to construct an equilibrium geochemical model that predicts the dominant uranium specie in the surface water. This information, along with analytical results on leachable iron, manganese and uranium produced from the subsurface-soil samples, was used to evaluate the degree of uranium retardation (if any) by the sediment and soil beneath Paddy's Run and the storm-water-outfall ditch. The analytical results for subsurface-soil samples were used to investigate three cases:

- No attenuation of uranium as it passes through the sediment and soil into the underlying aquifer (i.e., the vertical distribution of uranium in the subsurface-soil samples is similar to background levels)
- Uranium is historically bound-up in the subsurface-soil samples (i.e., uranium is retarded by the sediment and subsurface soil but has not broken through to the underlying aquifer)
- Uranium is present in the underlying aquifer solids (i.e., uranium has partially or completely broken through to the underlying aquifer)

These cases were evaluated by analyzing stream-bed borings obtained from Paddy's Run and the storm-water-outfall ditch for total uranium. Boring locations are shown in Figure 1. In Paddy's Run, one boring (P1; 1408) was placed upstream just below the waste-pit area and K-65 silos. A second boring (P2; 1409) was located in an area considered to be a significant zone of recharge to the underlying aquifer. The third boring (P3;1410) is downstream from the confluence with the storm-water-outfall ditch. These locations were chosen to allow a comparison of segments of Paddy's Run impacted by the flow from the storm-water-outfall ditch and those segments upstream from the confluence.

In the storm-water-outfall ditch, the upstream location (S1; 1405) was placed above the spillover of the storm-water-retention basin to evaluate the level of uranium retained by an inactive reach of the storm-water-outfall ditch. The second location (S2; 1406) is on an existing depression in the channel bottom, thought to be the remnants of a small, abandoned settling

basin. This area is proximal to the easternmost fly-ash pile and could serve to account for any associated impacts of fly ash on the storm-water-outfall ditch and underlying aquifer. A third boring (S3; 1407) is located near the confluence with Paddy's Run, which accounts for cumulative effects of fly-ash piles and/or whether most uranium is lost prior to reaching this point.

1.3.2 Analytical Methods and Field Sampling

International Technology Analytical Services (ITAS-Oak Ridge) analyzed surface waters for chemical and radiological parameters and subsurface soils for total uranium. In addition, the parameters Eh, pH, dissolved oxygen, conductivity, temperature and alkalinity were measured during the collection of samples. The collection, handling and analysis of subsurface soils and surface waters conformed to the procedures and conventions established in Revision 3 of the FMPC RI/FS Work Plan and Quality Assurance Project Plan (QAPP). Modifications to the collection and analysis of subsurface-soil samples were addressed in the Field Sampling and Laboratory Procedure Plan for the Geochemical Program. A summary of the field-sampling procedure appears below, and analytical methods are discussed in Section 2.0.

1.3.2.1 Field-Sampling Procedure for Subsurface Soils

Details on the procedures and conventions used for the collection, handling and analysis of subsurface soil samples can be found in Revision 3 of the FMPC RI/FS Work Plan and QAPP, and the Field Sampling and Laboratory Procedure Plan for the Geochemical Program. The field-sampling procedure is summarized as follows:

- Split-spoon samples were collected continuously in six-inch intervals from the stream bed surface to the sand- and gravel-aquifer water table
- Samples were two- to six-inch sections of the split-spoon core
- If the water table was not detected because of wet subsurface material throughout, borings were advanced to the following depths:
 - P1 (1408) to 24 feet
 - P2 (1409) to 20 feet
 - P3 (1410) to 20 feet
 - S1 (1405) to 34 feet
 - S2 (1406) to 17 feet
 - S3 (1407) to 9 feet

- Changes in lithology and/or geochemistry took precedence over the depth-interval sampling criterion (e.g., if iron staining begins at a depth of 12 feet, a new sample begins at 12 feet)
- The sample log recorded the percent recovery for a given 1.5-foot interval and any interval where soil was not recovered
- If the first or second split-spoon interval was refused, the boring was restarted from the ground surface
- Samples were bottled immediately after screening, and no samples were collected for volatile organic analysis (VOA), regardless of HNu or organic vapor analysis (OVA) reading
- Boring logs emphasized lithology, stratigraphy and geochemical descriptions
- A maximum of eight soil samples from each boring were sent to the laboratory for total uranium analysis
- Samples not analyzed were archived for future use, if necessary.

1.4 ISSUE FIVE: PARAMETERS FOR SOLUTE-TRANSPORT MODEL

1.4.1 Purpose and Scope

The purpose of issue five is to estimate a uranium distribution coefficient (K_d) for the sand and gravel aquifer. In developing a technical approach to satisfy this objective, the following assumptions were made:

- · The application of the solute-transport model is limited to the sand and gravel aquifer
- The relatively uniform characteristics of the sand and gravel aquifer imply related published information could provide K_d values without site-specific, laboratoryattenuation studies
- Only uranium is currently proposed for detailed consideration in the solute-transport model, and the K_d value for uranium is the focus of this issue.

Two methods were proposed to determine a uranium K_d value for the aquifer. The first method relied on analytical data from groundwaters as input to a geochemical equilibrium model (EQ3NR; Wolery, 1983) to predict the dominant uranium species in solution. This information was to be combined with mineralogic data on the sand and gravel aquifer and the two sets of site-specific data compared to results of published K_d studies. A second method was proposed to evaluate independently the uranium K_d by conducting laboratory sorption studies with the sand and gravel solids.

The first method was modified to exclude mineralogic identification of aquifer solids after initial geochemical modeling and aquifer-solid analyses indicated that the dominant uranium specie was $UO_2(CO_3)_3^{-4}$, a negatively-charged specie that would not exhibit significant sorption on clay minerals with high cation-exchange capacity. To resolve this problem, the analytical results on leachable iron were used to estimate the amount of amorphous iron (which has a strong affinity for negatively-charged complexes) that could be present as coatings on clay minerals and along fractures in the aquifer. Using these estimates, and a published study on uranium sorption by amorphous iron oxyhydroxide, empirical calculations were carried out to derive an apparent uranium K_d value.

The second method cited above has not been carried out at this time. However, an alternative method was substituted to maintain two independent calculations of the uranium K_d value. Using the total uranium values obtained on leachates derived from the leachable iron and manganese test, and uranium analyses of groundwater, a K_d was calculated directly from the uranium concentration in the solid (after a correction for background levels) and groundwater $[K_d = (mg \ U/kg \ solid)/(mg \ U/L \ groundwater)]$.

1.4.2 Analytical Methods and Field Sampling

ITAS-Oak Ridge performed the differential leaching/total uranium analysis of aquifer solids and the chemical and radiological analyses of groundwaters. Field parameters were measured on all groundwaters. To assist in determining the redox potential (Eh) of groundwater, 16 wells were sampled and analyzed for U⁺⁴ and total U (U⁺⁶ = total U - U⁺⁴). U⁺⁴ and U⁺⁶ are defined as the sum of all uranium species for each oxidation state. The U⁺⁴ and total U analyses were done by United Nuclear Corporation Geotech Laboratories (UNC Geotech), Grand Junction, Colorado. In support of the partitioning studies, IT-Export carried out analyses on the aquifer solids for total cation-exchange capacity, total organic carbon, grain size, and leachable iron and manganese. A leachate split was sent to ITAS-Oak Ridge for total U analysis.

The collection, handling and analysis of aquifer solids and groundwaters conformed to the procedures and conventions established in Revision 3 of the FMPC RI/FS Work Plan and Quality Assurance Project Plan (QAPP). Detailed procedures for the differential leaching analysis of aquifer solids, and U⁺⁴ and total U field sampling and analytical methods are given

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in the Appendix of the Field Sampling and Laboratory Procedure Plan for the Geochemical Program. A summary of the U⁺4 and total U field-sampling procedure appears below, and analytical methods are discussed in Section 2.0.

1.4.2.1 Field-Sampling Procedure for U+4 and Total U

Groundwater samples were collected for total U and U⁺4 analysis to estimate independently the Eh of the groundwater. The U⁺⁴ in solution is complexed with cerium and precipitated with hydrofluoric acid. U⁺⁶ is determined by the difference of total U and U⁺⁴. The procedure is summarized as follows:

- Approximately 250 ml of sample is collected after filtering the groundwater through a 0.45 um filter
- The sample is split and half is acidified with HNO₃ to pH<2 and shipped to the laboratory for total U analysis
- 25 ml of the remaining filtered sample is placed into a 125 ml plastic bottle, and 0.125 ml of cerium solution is added to the sample and mixed well
- 1.25 ml of reagent grade HF is added to the solution, and the solution is mixed thoroughly and cooled for 15 minutes in a cooler
- The sample is removed from the cooler, shaken, and filtered through a 0.1 um filter
- The sample bottle is rinsed three times with distilled water and the rinse solution is passed through the 0.1 um filter
- The filter funnel and filter paper are rinsed with distilled water prior to placing the filter paper in a container for shipment to the laboratory, where it is analyzed for U+4.

2.0 ANALYTICAL METHODS AND RESULTS

2.1 ANALYTICAL METHODS

Standard analytical methods (e.g., Methods for Chemical Analysis of Waste and Water; EPA-600 4-79-020) were used for the analysis of surface waters and groundwaters and will not be discussed here. Subsurface soils and aquifer solids were analyzed by gamma spectrometry for total uranium. Aquifer solids were also subjected to leaching tests to determine the amount of leachable iron, manganese and uranium. Leachates recovered from these tests were analyzed for iron, manganese and uranium by standard procedures (e.g., atomic absorption, inductively

coupled plasma or laser fluorimetry). Some of the analytical methods employed for subsurface soils and aquifer solids are site-specific applications and are summarized below. Detailed laboratory procedures for the leaching tests can be found in Revision 3 of the FMPC RI/FS Work Plan, the Work Plan for the Geochemical Program and the Field Sampling and Laboratory Procedure Plan for the Geochemical Program.

2.1.1 Gamma Spectrometry

Solid samples analyzed by the gamma-spectrometry method are generally 500 gram splits of crushed and homogenized material. After sample preparation is completed, the samples are placed in containers that will yield an analytical geometry identical to that of standards used to calibrate the instrument. The standards have known concentrations of each uranium isotope that emits gamma radiation and are used to construct a calibration curve prior to sample analysis. Most instruments used for this procedure employ sophisticated software that contains a complex algorithm to account for sample-instrument geometry, sample weight, the coefficient of absorbance for gamma radiation in the sample material, and interfering gamma radiation from other radionuclides present in the sample. The sample geometry and weight are given as input parameters prior to analysis and the algorithm calculates the total uranium concentration in the sample based on the contribution of each uranium isotope. Output from the algorithm is the total uranium concentration in ug/g (ppm).

2.1.2 Differential Leaching Tests for Uranium

The differential leaching tests distinguish between easily mobilized and available uranium (i.e., sorbed or amorphous uranium phases) from insoluble uranium (i.e., U in mineral lattices such as zircon) that is not available to the groundwater environment. The four leaching tests are designed to provide the following information:

- Uranium present in fine-grained carbonate minerals (i.e., pore cement)
- Uranium present as sorbed species on clay minerals and amorphous iron and aluminum oxyhydroxides
- Uranium present as sorbed species or within organics in the soils or wastes
- Uranium present in amorphous solids or oxide phases such as UO₂ or U₃O₈.

The uranium of most concern is probably bound on amorphous iron and aluminum oxyhydroxides that coat clay minerals, or is present with the organics and amorphous oxide phases. This uranium (if present) could be available for transport through the aquifer. Uranium which is present in the lattices of clay minerals, apatite, monazite and zircon is naturally occurring and generally immobile, and can be considered representative of the background concentration level.

The four-step extraction technique can be summarized as follows:

- Sodium acetate is used to digest the fine-grained carbonate minerals
- Disodium ethylenediaminetetracetic acid (EDTA) is used to strip sorbed uranium from clay minerals, and amorphous iron and aluminum oxyhydroxides
- Hydrogen peroxide is used to digest organic material
- Nitric acid (1:1 with distilled H₂O) is used to dissolve amorphous solids and oxides of uranium.

At each step, the reagent is agitated with the sample and the solution fraction (leachate) was recovered by centrifuging. The leachates were analyzed for total uranium by laser fluorimetry.

2.1.3 <u>Leaching Technique for Iron and Manganese</u>

This leaching technique recovers iron and manganese from amorphous-oxyhydroxide coatings on grains or fractures and crystalline oxide minerals using a solution of acetic acid and hydroxylamine hydrochloride. The solid is mixed with the leaching solution, agitated and the leachate recovered by centrifuging. Unlike the differential leaching procedure which recovers 'historical' uranium (i.e., recently bound uranium) this procedure will also recover ancient uranium locked in the mineral lattices of detrital grains or fracture coatings. Therefore, uranium sorbed to iron- and manganese-oxyhydroxide coatings on grain surfaces or fractures is removed and mixed with uranium recovered from the lattice sites in iron- and manganese-oxide minerals (i.e., detrital grains or fracture coatings of hematite or pyrolusite). The two uranium components cannot be distinguished in the analysis, and the background component (i.e., uranium in mineral lattices) must be estimated from aquifer solids which are known to be uncontaminated.

2.2 ANALYTICAL RESULTS

Analytical results for samples of subsurface soils, surface waters, aquifer solids and groundwaters are given in Appendix A. Groundwater analyses reported in Appendix A are limited to the samples chosen for geochemical modeling. The analytical results for uranium on subsurface-soil and surface-water samples obtained from Paddy's Run and the storm-water-outfall ditch were used to evaluate a source term for these drainages (issue three). Analytical results on groundwaters and aquifer solids were used to calculate apparent uranium distribution coefficients for the sand and gravel aquifer (issue five).

2.2.1 Issue Three

Analytical results for total uranium were obtained on subsurface soils and surface waters in Paddy's Run and the storm-water-outfall ditch to evaluate a source term for these drainages.

2.2.1.1 Subsurface Soils

Samples of subsurface soils obtained from Paddy's Run and the storm-water-outfall ditch (Fig. 1) were analyzed for total uranium by gamma spectrometry. The samples consist primarily of well-graded sand and gravel with horizons of poorly-graded sand and silty clay. Borehole depth ranged from 20 to 24 feet and 9 to 34 feet, respectively, in Paddy's Run and the storm-water-outfall ditch. The deepest borehole in the storm-water-outfall ditch (S1; 1405) penetrated an iron- and manganese-stained horizon between 25 and 30 feet below the surface, which was interpreted as a possible redox zone. Uranium results for six of the sampling sites are illustrated in Figures 2 and 3.

Soil samples recovered from Paddy's Run (Fig. 2) had total uranium concentrations of less than 1 to 4 ug/g (ppm). However, significant 2-sigma counting errors (generally > 50 % and up to 100 % of the reported value) precludes any discussion of significant variation in the uranium concentration with depth (i.e., no variation observed within the range of 2-sigma counting errors; Fig. 2). Additionally, for uranium concentrations in these soil samples, it is not possible to separate components of contamination (if present) from regional background levels, which in common rocks are: carbonates, 2.2 ppm; shales, 3.7 ppm; and granites, 5 ppm (Faure, 1977; Krauskopf, 1979). Site environmental-monitoring data has established uranium background levels of 1 to 3 ppm in the aquifer solids.

Total uranium values for soil samples recovered from the storm-water-outfall ditch ranged from 1 to 10 ppm (Fig. 3). Large 2-sigma counting errors makes discussion of uranium variation with depth equivocal for site S3 (1407). However, the soil profiles from sites S1 (1405) and S2 (1406) show uranium variation that is significant (i.e., greater than 3 ppm). Site S1 (1405) is most proximal to the Fernald compound (Fig. 1) and is located above the spillover for the storm-water-retention basin. Soil samples recovered from this boring indicate a decrease in the uranium concentration from 10 to 4 ppm within the top 4 feet of soil (Fig. 3). The high uranium concentrations in the upper 3 feet of this boring coincide with a clay-rich horizon between 0.5 and 2 feet, suggesting uranium may have sorbed onto the clay (see Section 2.5.1).

Site S2 (1406) is located near a fly-ash pile and in a depression which may be an abandoned settling basin. Very little (if any) soil is present at site S2 (1406), and the boring penetrates the top of the sand and gravel aquifer. The uranium profile from this site indicates uranium concentrations of 6 to 8 ppm over the interval of 5 to 15 feet (background uranium is less than 3 ppm). Because the soil present at this site is negligible, the profile indicates 'historical' uranium is present in the aquifer.

2.2.1.2 Surface Waters

Analytical results for three surface-water samples (W-7, W-11 and ASIT003; sampled 05/14/89) are given in Appendix A. Samples were collected in each flowage above the confluence of Paddy's Run and the storm-water-outfall ditch (W-11 and ASIT003, respectively), and below the confluence (W-7; Fig. 1). The surface samples are oxygenated waters (Eh approximately 450 mV) with a pH of about 8.5 and their solution chemistry is dominated by HCO₃⁻ (> 200 mg/L) and Ca (> 70 mg/L), reflecting the interaction of these waters with carbonate rock in the subsurface. Uranium concentrations in the surface-water samples ranged from 0.002 (ASIT003) to 0.015 (W-07) mg/L. The sample obtained from the storm-water-outfall ditch (ASIT003) has a uranium concentration similar to background levels established for Paddy's Run (0.001 to 0.004 mg/L), using site-specific environmental-monitoring data. Samples recovered from Paddy's Run, above and below the confluence with the storm-water-outfall ditch, have uranium concentrations above the background level maximum, indicating these surface waters might

contribute uranium to the underlying aquifer by vertical infiltration. Modeling results for uranium speciation are presented in Section 3.3.

2.2.2 Issue Five

Analytical results for total uranium were obtained on aquifer solids and groundwaters to calculate an apparent distribution coefficient $[K_d = (mg \ U/kg \ solid)/(mg \ U/L \ groundwater)]$ for the sand and gravel aquifer. Additionally, geochemical modeling on the speciation of uranium in groundwater was combined with analytical results on leachable iron to derive empirically a distribution coefficient.

2.2.2.1 Aquifer Solids

Thirty-one subsurface samples consisting of gravel, sand, silt and clay were analyzed for leachable iron, manganese and uranium, total organic carbon, total cation exchange capacity and grain-size variation. Thirteen of these sample were also utilized for total uranium analysis (6) and differential-leaching uranium analysis (7). Analytical results are given in Appendix A and illustrated in Figures 4 to 6.

Figure 4 is a plot of leachable iron, manganese and uranium against the particle size of the sample. Based on the sieve analysis, two sample populations exist: (1) silt + clay greater than 50 weight percent and (2) silt + clay less than 25 weight percent. The leachable fraction of iron, manganese and uranium in the majority of aquifer-solid samples is not a function of the particle size, because the range of values for the metals is similar for the two sample populations. This observation suggests that the majority of iron and manganese solids accessed by the groundwater are present as amorphous- or crystalline-oxyhydroxide coatings along fractures in the fluid-flow path, rather than as detrital grains or surface coatings on the aquifer particles. This hypothesis is consistent with sample preparation procedures which avoided crushing the sample below its natural aggregated size (i.e., clay minerals were not mechanically disaggregated prior to the leaching test).

Three clay samples in the first population have leachable iron values greater than 2 mg/g, suggesting surface coatings on clay minerals and/or complexation with organic-carbon (see

below) controls the leachable fraction of iron in these samples. A lack of correlation between the sum of leachable iron and manganese versus total uranium (inset Fig. 4) indicates that:

- Sorption of uranium on amorphous iron- and manganese-oxyhydroxide coatings may not be occurring in the aquifer or
- The leachable iron and manganese in the solids is primarily from the digestion of crystalline oxyhydroxide phases.

Results for total organic carbon versus grain size are illustrated in Figure 5. As in Figure 4, there is no correlation between the total-organic-carbon content of the aquifer solids and the weight percent of silt and clay in the sample. The majority of samples, irrespective of silt and clay content, have total-organic-carbon values below 8 mg/g. Two samples obtained from a major clay interbed in the sand and gravel aquifer contain 15 to 16 mg/g of total organic carbon. These two samples are coincident with the highest leachable iron values in Figure 4. The correlation of high organic carbon content to high leachable iron values implies iron is associated with or adsorbed on organic materials in the clay interbed.

In contrast to results presented in Figures 4 and 5, the cation exchange capacity of the aquifer solids is a strong function of the silt and clay content (Fig. 6). Samples containing less than 25 weight percent of silt and clay have a total cation exchange capacity (CEC) of less than 0.04 meq/g, whereas those samples with greater than 50 weight percent silt and clay have CEC up to 0.28 meq/g.

2.2.2.2 Anomalous Uranium Results

Thirteen aquifer-solid samples were chosen for total-uranium analysis by gamma spectrometry. Seven of the 13 samples were selected for a differential-leaching procedure designed to strip uranium sequentially from the solids using a series of four progressively stronger leaching reagents (see analytical methods in the Appendix of the Field Sampling and Laboratory Procedure Plan for the Geochemical Program). Results for the total-uranium and differential-leaching analysis are reported in Appendix A and illustrated in Figures 7 and 8. It is emphasized that these results are anomalous with respect to those obtained previously for total uranium of aquifer solids.

Figure 7 is a plot of total uranium (ug/g or ppm) versus sample depth for six of the thirteen samples. Mean uranium concentrations in these aquifer solids range from about 11 to 16 ppm, but show no variation within their 2-sigma counting errors. The mean uranium values are about 3 to 5 times higher than the maximum uranium background level of 3 ppm (based on uranium analyses of subsurface solids from uncontaminated wells). Possible causes of the elevated uranium values are:

- · Uranium sorption on particles along the flow path
- Precipitation of uranium solids along the flow path
- The presence of naturally-occurring uranium-bearing minerals (i.e., zircon, apatite or monazite) in the aquifer sands
- Problems with the procedures and analytical methods used to determine the uranium concentration (see Section 2.5.2).

Uranium results from the differential-leaching procedure are shown in Figure 8. The seven samples analyzed had mean uranium concentrations of 95 to 150 ppm prior to leaching and, within their 2-sigma counting error, were unchanged after leaching. Additionally, sample-to-sample variation in uranium concentration is not observed within the 2-sigma counting error. These solids have uranium concentrations 1 to 2 orders of magnitude higher than background uranium concentrations (see above), and an order of magnitude higher than the results shown in Figure 7. Sorption and precipitation of uranium along the flow path cannot be responsible for the high concentrations in these samples, because the leachates (analyzed by laser fluorimetry) from the solids had less than 2.5 ppb of uranium. Likewise, the uranium-bearing mineral apatite, and to a lesser degree monazite, cannot contribute significantly to the high uranium concentrations because they are soluble in nitric acid (used in final leaching step). The results presented in Figure 8 can be explained by high concentrations of insoluble uranium-bearing minerals (i.e., zircon) in the aquifer sands or problems with the analytical procedures and methods (see Section 2.5.2).

2.2.2.3 Groundwaters

Analytical results for groundwater samples used in the geochemical modeling appear in Appendix A. These groundwaters were collected from 20 monitoring wells (locations shown in Fig. 9) during Round 3 (Fourth Quarter, 1988) and Round 4 (First Quarter, 1989) sampling.

The dominant chemical characteristics of the groundwaters include: near-neutral pH values (6 - 8), Eh values of 50 to 450 mV, HCO₃⁻ concentrations of 200 to 400 mg/L, and Ca concentrations of 70 to 200 mg/L. These chemical characteristics suggest the groundwaters are in equilibrium with carbonate rocks in the aquifer. Uranium concentrations in these samples vary from 0.005 to 4.38 mg/L, with most modeling samples having concentrations greater than expected for natural waters (i.e., U > 0.0001 to 0.010 mg/L; Hem, 1970). Modeling results for the uranium speciation are presented in Section 3.3.

2.3 DISCUSSION

2.3.1. Issue Three

Uranium concentrations in most subsurface-soil samples overlap with the range of values reported for common rock types (i.e., 2-5 ppm) and do not appear to reflect the sorption and/or precipitation of uranium from infiltrating groundwater. The lack of uranium contamination in the majority of the soil samples suggests any one or all of the following:

- · The soils were not exposed to uranium-bearing water
- Uranium that had sorbed onto the soils has been subsequently desorbed by uncontaminated water
- Uranium was in the form of non-sorptive species.

Therefore, the soil profiles from sites P1 (1408), P2 (1409), P3 (1410), and S3 (1407) may conform to the case one scenario (Section 1.3.1), which states that if surface waters with high uranium concentrations infiltrated these soils, no attenuation took place (i.e., the soil profile for uranium reveals background levels). This scenario supports the speciation results for surface waters (Section 3.3, Table 2), which indicate the neutral complex UO₂(H₂PO₄)₂* is present and little (if any) attenuation of uranium will occur as surface waters vertically infiltrate to the underlying aquifer. The scenario also supports modeling results which indicate the anionic uranyl-carbonate species are present if amorphous iron oxyhydroxide is absent (i.e., no sorption on the soil-particles).

Exceptions are sites S1 (1405) and S2 (1406). At site S1 (1405), uranium values up to 10 ppm in the upper 2-3 feet of soil suggest uranium sorption and/or precipitation may have occurred.

Site S1 (Fig. 3) is proximal to the discharge point for the storm-water-outfall ditch, and higher uranium concentrations in these subsurface-soil samples are in agreement with known periodic discharges of uranium-bearing waters. The elevated uranium concentrations in the upper 3 feet of this boring are coincident with a clay rich horizon between 0.5 and 2 feet. This observation suggests that uranium is being retarded by sorption processes in this area. Therefore, this uranium is a potential source for future releases to the underlying aquifer.

Site S2 (1406) shows slightly elevated uranium concentrations (6 to 8 ppm) over a depth interval of 5 to 15 feet. However, this observation cannot be correlated with clay-rich horizons found in the soil profile at site S1, because little (if any) soil is present at this site. This site is proximal to a fly-ash pile and may also be situated on the remnants of an abandoned settling basin. Either of these observations could account for the presence of 'historical' uranium in the S2 profile. Uranium may be retarded along this profile by sorption onto iron- and manganese-oxyhdroxide coatings, which formed along the fluid-flow path, or by precipitation of amorphous uranium compounds. Because site S2 (1406) is located in an area where the till is absent, this uranium is currently present in the aquifer, and is a potential source for future release and transport through the aquifer.

The soil profile from site S1 (1405) supports the case two scenario (Section 1.3.1), which states that uranium present above the expected background level is 'historical' uranium bound in the subsurface soil (i.e., no breakthrough has occurred to the underlying aquifer). However, the profile from site S2 (1406) indicates partial breakthrough of uranium to the sand and gravel aquifer (case three, Section 1.3.1). For both of these cases, modeling results which predict the dominant uranium specie as $UO_2(CO_3)_3^{-4}$ (Section 3.3, Table 2) support the hypothesis of uranium sorption on amorphous iron- and aluminum-oxyhydroxide films. Alternatively, uranium may be retarded by precipitation of amorphous uranium compounds.

2.3.2 Issue Five

Analytical results for uranium concentrations in aquifer solids are highly suspect because the differential-leaching procedure did not lower uranium values in aquifer solids that are 1 to 2 orders of magnitude larger than background uranium concentrations. Those samples which did

not undergo the differential-leaching procedure had uranium concentrations 2 to 8 times higher than common rocks, but are also suspect because the differential-leaching procedure indicates a lack of sorbed or amorphous uranium (i.e., all uranium present is within mineral lattice structures), which is in contrast to uranium results obtained on leachates derived from the iron and manganese experiments (see below). Petrographic data on the composition of aquifer sands is not available, although it is unlikely that high concentrations of an insoluble uranium-bearing phase such as zircon would be found to account for the elevated uranium concentrations. The most probable cause of the anomalously high uranium concentrations is a variation in the standard analytical procedure or method.

Gamma spectrometry is used to analyze for total uranium in the aquifer solids. This analytical method is sensitive to the mass of solid analyzed and the geometry of the sample with respect to the detector. Standards used to calibrate the instrument are 500 gram aliquots that are dried and ground to homogenize the solid prior to analysis. Aquifer-solid samples of 4 to 40 grams were analyzed without drying and homogenizing the material, and the small sample volumes resulted in poor geometry configurations with respect to the detector. These deviations from standard procedures requires that the analytical results for total uranium in aquifer solids be treated as qualitative.

In contrast, the total uranium in the leachate fractions produced from the differential-leaching procedure were analyzed by laser fluorimetry and results are considered to be quantitative. These results indicate that less than 2.5 ppb of uranium is sorbed onto the aquifer solids, which is in contrast to uranium values of 33 to 783 ppb obtained from the leachate produced by the iron- and manganese-oxyhydroxide stripping procedure. Reagents specific to each procedure can account for the difference in uranium results, as the analytical method was identical for all leachates. The differential leaching is a four-step procedure; initial leaching with sodium acetate followed by EDTA, hydrogen peroxide, and nitric acid solutions. This procedure removes:

- Uranium sorbed to inorganic and organic particles
- Uranium complexed within amorphous aluminum, iron or manganese oxyhydroxides
- Amorphous uranium solids present in the sample.

In contrast, the iron- and manganese-oxyhydroxide procedure utilizes acetic acid and hydroxylamine hydrochloride to attack amorphous and crystalline iron- and manganese-oxyhydroxide minerals (Chester and Hughes, 1967). Therefore, the latter procedure will contain a uranium component derived from crystallized iron and manganese minerals (i.e., detrital minerals older than the Holocene), while the former will not. The uranium in the detrital minerals is not of recent origin, and the concentrations of less than 1 ppm are well below the average of 3.7 ppm reported for shales (Krauskopf, 1979).

Because of the suspect nature of the uranium analytical results for aquifer solids and leachates, calculated distribution coefficients (K_d) should be interpreted cautiously. However, the calculations are useful as an independent check on partitioning estimates based on speciation modeling (Section 3.3) and experimental studies (Section 4.1).

3.0 GEOCHEMICAL MODELING

Geochemical modeling of the uranium speciation in surface waters was carried out to assist in the evaluation of the potential source term in Paddy's Run and the storm-water-outfall ditch (issue three), and in groundwaters to support the calculation of the uranium distribution coefficient for the aquifer (issue five). Modeling was conducted with the EQ3NR geochemical code (ver. 3245; Wolery, 1983), which is an industry standard, speciation/solubility code developed by Lawrence Livermore National Laboratory for use in predicting the behavior of metals, radionuclides, and other contaminants in the natural environment. The code accesses a data base containing the thermodynamic properties of 47 elements, 686 aqueous species, 713 minerals, and 11 gases. This data base includes 49 uranium-bearing aqueous species and 53 uranium-bearing minerals, constituting the most complete data base available for modeling the behavior of uranium in natural waters.

Modeling results must be interpreted cautiously. Values for thermodynamic parameters utilized by the EQ3NR code for speciation and solubility calculations are experimentally determined by many investigators, and the quality of their results is variable. Personnel at Lawrence Livermore National Laboratory have qualified the thermodynamic data utilized by the code by

indicating whether the data is poor, fair, good or uncertain. Uncertain generally indicates that independent workers have reached conflicting results for the indicated value and the problem is currently unresolved. All aqueous-uranium species and uranium minerals considered in this investigation have thermodynamic values which have been judged to be good.

Additionally, it must be emphasized that results obtained from geochemical modeling of natural systems are not unique. At best, modeling can present a snapshot of a point in time for the dynamic natural system. However, modeling studies are useful to establish boundary conditions for a system, which may enhance the development of remediation techniques and/or the solution to contaminant problems.

3.1 SELECTION CRITERIA FOR GROUNDWATER SAMPLES

Over 100 groundwater analyses from Round 3 (Fourth Quarter, 1988) and Round 4 (First Quarter, 1989) were available for modeling. Because of the large number of analyses received, selection criteria were developed to choose samples from the entire spectrum of analyses, thus reducing the number of analyses to model. All groundwaters with reported uranium concentrations greater than 0.3 mg/L (7 analyses) were modeled. Analyses deemed to be representative of 'typical' local groundwaters were screened for uranium content, and 14 samples were chosen that had uranium concentrations of 0.005 to 0.3 mg/L (greater than 50 percent of the samples received had reported uranium concentrations of less than 0.005 mg/L). Additional criteria focused on anomalous concentrations of calcium, phosphorous, potassium and sulfate, and Eh values (based on platinum electrode measurements) that were below 100 mV (6 analyses). It is important to reiterate that the selection criteria for groundwater samples used in the geochemical modeling is biased toward those analyses with high uranium concentrations.

3.2 MODELING ASSUMPTIONS AND CONSTRAINTS

Analytical results received for surface and groundwaters did not contain values for total dissolved solids (TDS) and specific gravity (SG). Many results also lacked a reported value for the redox potential (Eh) of the water. Values for these parameters must be included on the input file for the EQ3NR code and were estimated as follows:

- TDS was calculated by summing the concentrations (in mg/L) of analytes that were above the detection limit
- SG was assumed to be 1 g/cc, based on the low TDS values (400 600 mg/L)
- Eh was calculated by the EQ3NR code using the NH₄⁺/NO₃⁻ and O₂/H₂O redox couples, and with solubility constraints based on pyrolusite (MnO₂) and uraninite (UO₂) saturation (Eh calculations are discussed in detail in Section 3.2.2).

3.2.1 Electrical Charge Imbalances

The 26 water analyses utilized for modeling had electrical charge balances ranging from -27 to +64 percent of the total charge (Table 1). About half of the analyses have reasonable charge balances that lie between -5 and +5 percent of the total charge. Electrical imbalances greater than +5 or less than -5 percent suggest either errors in the analysis of a major constituent or the omission of a major constituent in the analysis. The omission of a major constituent will usually cause a consistent bias (positive or negative) in the electrical imbalance, thus the range of imbalances observed here suggests random errors in the analyses. A reduced level of confidence should be placed on those analyses with large electrical imbalances (i.e., those that lie outside of the range -5 to +5 percent) and the corresponding uranium speciation calculated from the analytical data. However, uranium speciation will probably not be affected by large electrical imbalances resulting from analytical errors in the determination of calcium, potassium, magnesium, sodium or sulfate, but can be affected if the phosphorous concentration, alkalinity, or pH is in error (see discussion of uranium speciation in Section 3.3).

3.2.2 Eh Calculations

Platinum-electrode measurements were not provided with all groundwater analyses and a variety of redox couples and mineral-solubility limits were utilized to constrain the system Eh. Eh values were calculated with the O_2/H_2O (770 to 800 mV), NH_4^+/NO_3^- (324 to 350 mV) and U^{+4}/UO_2^{+2} (-120 to -160 mV) redox couples, and by lowering the O_2/H_2O redox value in increments until the solution reached saturation with respect to, first, pyrolusite (MnO₂; 575 to 605 mV) and then uraninite (UO_2 ; 35 to 50 mV). Eh values bounded by the pyrolusite and uraninite solubility limits overlap with the range obtained by platinum-electrode measurements in the field (454 to 75 mV).

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The O_2/H_2O and U^{+4}/U^{+6} redox couples overestimated and underestimated, respectively, the redox state of the groundwaters. For the O_2/H_2O couple, the high Eh value may be due to addition of atmospheric O_2 during sample collection or the inability of the geochemical code to evaluate the kinetic rate of the O_2 - H_2O half-cell reaction. Calculation of the groundwater Eh with the U^{+4}/U^{+6} couple produced values inconsistent with mineral solubilities and platinum-electrode measurements. Low uranium redox values (-120 to -160 mV) indicate concentrations of U^{+4} are too high. The high U^{+4}/U^{+6} ratios measured in these groundwaters are attributed to the sorption of uranyl species on iron-bearing colloids (Fig. 10), which comprised a portion of the filtered residue analyzed for U^{+4} (see field sampling technique for U^{+4} and total U in Field Sampling and Laboratory Procedure Plan for the Geochemical Program).

Because a wide range of Eh values were used to model uranium speciation, several groundwater compositions were modeled over an Eh range of 50 to 650 mV to determine the affect (if any) of Eh variation. Results for this test are shown in Figure 11, and indicate that variation in the Eh estimate of groundwaters does not affect the speciation results for uranium.

3.3 **URANIUM SPECIATION**

Uranium speciation was investigated in 26 groundwater samples (20 unique wells) and 3 surface-water samples. Results for the speciation modeling are presented in Tables 1 and 2. Speciation results for the groundwaters support calculations to estimate a uranium distribution coefficient for the aquifer (issue five). Table 1 reveals that 11 samples had greater than 99 percent of the uranium partitioned into the aqueous specie $UO_2(H_2PO_4)_2^*$, 9 samples (phosphorous not reported or below the detection limit) had greater than 99 percent of the uranium partitioned into the aqueous species $UO_2(CO_3)_3^{-4}$, $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)^*$, and 6 samples (five with uranium greater than 0.3 mg/L) partitioned the uranium into a combination of the above three species. These results indicate that uranyl ion (UO_2^{+2}) will form negatively charged complexes with carbonate ion (CO_3^{-2}) in this environment only if the molar concentration (moles per liter) of uranium is greater than one-half the molar concentration of phosphorous (i.e., [U] > 0.5[P]). When uranyl-carbonate complexes form, $UO_2(CO_3)_3^{-4}$ is the dominant specie in these groundwaters at neutral and slightly alkaline pH.

Three surface waters were chosen for uranium-speciation modeling to evaluate the potential of introducing uranium to the underlying aquifer by vertically infiltrating surface waters (issue three). Analyses for these three samples reported uranium concentrations of 0.002 to 0.015 mg/L, with phosphorous ranging from below the detection limit (<0.02 mg/L) to 0.16 mg/L (Appendix A). Because of the relatively low uranium concentrations in these surface waters, all uranium was partitioned into the neutral phosphate complex in waters which contained detectable amounts of phosphorous (Table 2). Surface waters without reportable phosphorous concentrations (i.e., W-11; Table 2) partitioned uranium into the anionic carbonate complexes.

3.3.1 Discussion

Preliminary results on the feasibility of recovering uranium from groundwaters by anion-exchange processes show 90 percent of the uranium is recovered by this method (personal communication, Khan, 1989). The experimental results are in good agreement with the majority of modeling results (i.e., negatively-charged uranyl-carbonate species). However, modeling results also indicate that uranium is complexed as the neutral $UO_2(H_2PO_4)_2^*$ specie in 11 of 26 groundwaters.

Several factors could account for the observed sorptive behavior of uranium. First, phosphorous (measured as total P and converted to phosphate) may form organic complexes in the groundwaters, which would reduce the activity of the phosphate complex and decrease the amount of $UO_2(H_2PO_4)_2^*$ formed. Organic-phosphate speciation was not modeled because thermodynamic data is limited to inorganic-phosphate complexes, which results in $UO_2(H_2PO_4)_2^*$ concentrations that may be over estimated. Second, the association constant for $UO_2(HPO_4)_2^{-2}$ may not be correct (see 3.3.1.1 below) and, therefore, significant partitioning of uranium into this specie cannot be ruled out. The presence of $UO_2(HPO_4)_2^{-2}$ in the groundwaters would be consistent with removal of uranium by anion exchange. Finally, the $UO_2(H_2PO_4)_2^*$ specie may exhibit weak dipole properties (similar to H_2O) that, despite the neutral charge, result in retardation along the flow path in an anion-exchange column.

3.3.1.1 Data Base Integrity

The speciation results for surface and groundwaters indicate that the uranyl ion has a strong affinity to form an uncharged complex with phosphate. A phosphorous concentration of 0.02

mg/L (the limit of detection) would allow up to 0.071 mg/L uranium to be complexed as $UO_2(H_2PO_4)_2$. Since the majority of analyses received (not modeled) have uranium concentrations less than 0.071 mg/L and phosphate values greater than 0.02 mg/L, the modeling results suggest carbonate complexation may not occur in these groundwaters. However, the speciation results for groundwaters containing phosphorous appear to be in conflict with published studies (Scanlan, 1977; Tripathi, 1984; Koss, 1988), which indicate UO_2^{+2} will form carbonate complexes in bicarbonate waters at neutral pH. In addition, studies by Moskvin et al. (1967) and Dongarra and Langmuir (1980) concluded that the dominant uranyl-phosphate complex in natural waters of neutral pH is the single-protonated, negatively-charged $UO_2(HPO_4)_2^{-2}$ complex, which is in contrast to the neutral, double-protonated $UO_2(H_2PO_4)_2^{-2}$ specie predicted by the EQ3NR code.

To resolve this apparent discrepancy, the thermodynamic values for the aqueous uranium species active in this study were checked to ensure data base integrity. Association constants for $UO_2(H_2PO_4)_2$ (log K = 45.24; Baes, 1956; Tripathi, 1984), $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$ (log K = 17.08 and 21.70, respectively; Scanlan, 1977; Tripathi, 1984)) were verified to be correctly entered in the thermodynamic data base. However, single-protonated uranyl-phosphate complexes (e.g., UO2HPO4* and UO2(HPO4)2-2) were not present in the thermodynamic data base. Lawrence Livermore National Laboratory removed singleprotonated uranyl-phosphate complexes from the EQ3NR data base as a result of the conclusions reached by Tripathi (1984). Tripathi argued that the studies of Moskvin et al. (1967) and Dongarra and Langmuir (1980), who concluded that ${\rm UO_2(HPO_4)_2}^{-2}$ (association log K = 18.3) is the dominant specie in oxygenated waters with pH between 4 and 8, are not valid because their experiments were carried out with acidic solutions (pH = 0 to 4) and uranyl complexation with H2PO4 and H3PO4 was not considered. The omission of the singleprotonated uranyl-phosphate complex from the data base was hypothesized to be insignificant because of the much larger association constant for UO₂(H₂PO₄)₂* relative to UO₂(HPO₄)₂-2 ($\log K = 45.24$ versus 18.3, respectively). This hypothesis was verified by reinserting the thermodynamic data of Dongarra and Langmuir (1980) into the data base and finding no change in the speciation after rerunning several groundwaters.

4.0 URANIUM ADSORPTION

Partitioning of uranium between aquifer solids and groundwater was evaluated to calculate an apparent distribution coefficient [$K_d \approx (mg \ U/kg \ solid)/(mg \ U/L \ groundwater)$] for uranium in the sand and gravel aquifer. This task was carried out to meet the objectives of issue five. Uranium adsorption was evaluated by:

- Modeling the uranium speciation of groundwater using the EQ3NR geochemical code and comparing the speciation output to published $K_{\mbox{\scriptsize d}}$ studies
- Calculating distribution coefficients based on uranium concentrations reported for archived aquifer solids, leachates, and groundwaters.

4.1 SPECIATION AND EXPERIMENTAL STUDIES

Speciation results presented in Section 3.3 indicate the expected uranium complexes in groundwaters recovered from Fernald monitoring wells are dominantly $UO_2(CO_3)_3^{-4}$ and $UO_2(CO_3)_2^{-2}$, and $UO_2(H_2PO_4)_2^{\bullet}$ when phosphorous is present. The modeling results are in good agreement with studies by Ferri et al. (1981), which show uranium is present as the $UO_2(CO_3)_3^{-4}$ complex in carbonate solutions between pH 7 and 12. Neutral aqueous species (e.g., $UO_2(H_2PO_4)_2^{\bullet}$) are not expected to sorb appreciably (perhaps slightly if the molecule has a strong dipole) and, consequently, are not considered in experimental studies. Therefore, this discussion focuses on studies which have addressed the adsorption of uranium from carbonate solutions.

4.1.1 Adsorption of Uranyl-Carbonate Species by Montmorillonite

Canterford and Sparrow (1983) studied the adsorption of uranium using a montmorillonite and carbonate solution mixture. A simple solution was prepared by adding 4 g of Na_2CO_3 and 8.4 g of $UO_2(NO_3)_2 \cdot 6H_2O$ to one liter of distilled water, yielding CO_3^{-2} and U concentrations of, respectively, 2.26 g/L (0.038 mole/L) and 3.97 g/L (0.017 mole/L) at a final pH of 7.7. The montmorillonite suspension was 0.48 weight percent solids at a pH of 7.6. Five mI of the uranium solution was added to 195 mI of the montmorillonite suspension and samples were stirred and agitated for 96 hours. Results for this experiment indicate an apparent K_d for uranium of 65.78 L/kg at a final pH of 8.

However, the large K_d value for uranium in this simple system is suspect with respect to sorption of anionic uranyl-carbonate species by montmorillonite. Note that the experiments of Canterford and Sparrow (1983) had about 0.004 mole/L of excess uranium that could not be complexed as the specie $UO_2(CO_3)_3^{-4}$ (the dominant specie at pH = 8; Ferri and Salvatore, 1981). That is, the amount of carbonate ion in the system, 0.038 mole/L, requires only 0.0127 mole/L of the available 0.017 mole/L of uranium to form $UO_2(CO_3)_3^{-4}$. Therefore, the excess 0.004 mole/L of uranium could be present as the UO_2^{+2} specie, which would readily sorb to montmorillonite in these neutral and slightly alkaline pH waters because of its low zero point of charge (montmorillonite pH_{ZDC} = 2.5; Stumm and Morgan, 1981).

The pH at which a clay mineral surface has a zero point of charge (pH_{zpc}) is very important with respect to sorption of charged aqueous species. At a solution pH value below the pH_{zpc}, the surface of the clay mineral contains only free positively-charged sites, which would attract negatively-charged ions (e.g., $UO_2(CO_3)_3^{-4}$). Similarly, for solution pH values above the pH_{zpc}, a clay mineral surface will have only free negatively-charged sites and sorb positively-charged ions (e.g., UO_2^{+2}).

An alternate hypothesis for the large K_d value reported by Canterford and Sparrow (1983) is that uranium partitioning is balanced to allow for $UO_2(CO_3)_3^{-4}$ (U = 0.004 moles/L) and $UO_2(CO_3)_2^{-2}$ (U = 0.013 moles/L) complexation without UO_2^{+2} . If this latter hypothesis holds, then the large K_d value for this system suggests amorphous AlOOH and FeOOH (pH_{zpc} = 8.2 and 7.8, respectively; Stumm and Morgan, 1981) films on the montmorillonite surface are sorbing the anionic complexes. This latter scenario is less credible because the dominant uranium specie in the solutions of pH = 8 (Canterford and Sparrow, 1983) would have to be $UO_2(CO_3)_2^{-2}$, which is in contrast to the $UO_2(CO_3)_3^{-4}$ specie predicted by experimental studies (Ferri et al., 1981) and modeling results.

4.1.2 Adsorption of Uranyl-Carbonate Species by Amorphous Ferric Oxyhdroxide

Ames et al. (1983) investigated sorption of uranium on amorphous ferric oxyhydroxide (pH $_{\rm zpc}$ = 7.8 to 8.5; Stumm and Morgan, 1981) at 25° and 60°C from 0.01 molar (moles/liter) NaHCO $_{\rm 3}$ solutions over an initial uranium concentration range of 0.0001 to 0.00000055 molar (23.8 to

0.13 mg/L). Their amorphous ferric oxyhydroxide was prepared by mixing 1 ml of 0.1 molar FeCl₃ with 30 ml of 0.01 molar NaOH. Uranyl-carbonate solutions were added to the ferric oxyhdroxide precipitate to yield an iron mass to solution volume ratio of 0.279 g/L. Solutions and ferric oxyhydroxide were sealed in polypropylene tubes and agitated for seven days. Blanks containing uranyl-carbonate solutions but no ferric oxyhydroxide indicated less than 2 percent tube-wall sorption. A count on the initial and final solutions determined the sorbed uranium by difference. Apparent K_d values at 25°C and average final pH of 8.6 to 8.7 ranged from about 4,000 L/kg at U = 23.8 mg/L to about 26,000 L/kg at U = 0.13 mg/L The apparent K_d values increased to, respectively, 5,000 and 34,000 L/kg at 60°C.

The results of Ames et al. (1983) indicate a strong potential for sorption of anionic uranyl-carbonate species onto amorphous ferric-oxyhydroxide surfaces in slightly alkaline solutions (maximum loading = 3.116 moles U per kg ferric oxyhydroxide). However, these apparent K_d values were calculated for a simple system and do not take into account the presence of other ligands (e.g, SO_4^{-2} , PO_4^{-3} , etc) in natural waters. Sulfate and phosphate complexes would compete for the available anion sorption sites on ferric oxyhydroxide and lower uranium K_d values considerably, primarily due to the much greater concentrations of sulfate and phosphate, relative to uranium, in solution.

4.1.3 Empirical Determination of a Uranium Distribution Coefficient

Using the maximum uranium loading on ferric oxyhydroxide (3.116 moles/kg; Ames et al., 1983), an apparent K_d between aquifer solids and groundwater was calculated. The calculation is based on the following assumptions:

- Groundwater and aquifer solids are in equilibrium at 25°C
- The composition of the groundwater is the same prior to and at equilibrium
- All uranium is speciated into UO₂(CO₃)₃-4
- The experimentally determined maximum uranium loading on ferric oxyhydroxide (3.116 moles/kg) is taken as the total moles of anionic species that can be sorbed
- All Fe leached from the aquifer solids was in the form FeOOH
- Each sorption site on FeOOH is occupied by either HCO₃⁻, NO₃⁻, HPO₄⁻², SO₄⁻², or UO₂(CO₃)₃⁻⁴

• The affinity of a molecule to sorb on FeOOH is proportional to its charge and concentration.

Assumptions three and five may introduce the greatest uncertainty in the K_d calculation. For instance, modeling results for uranium speciation in groundwaters (Table 1) indicates $UO_2(H_2PO_4)_2$ and $UO_2(CO_3)_2^{-2}$ are important species in addition to $UO_2(CO_3)_3^{-4}$. This uncertainty can be estimated by comparing the calculated K_d value based on the assumptions above with that calculated for speciation based on modeling results (Table 3). Partitioning of all iron into amorphous ferric oxyhydroxide is the most tenuous assumption, as the analytical leaching technique is known to recover iron from both amorphous- and crystalline-oxyhydroxide phases, and it is not possible to distinguish between these two iron components. However, even if the partitioning of iron among these components was known, the K_d value would probably not decrease by more than a factor of two, and this uncertainty is probably no greater than uncertainties associated with the remaining assumptions.

Noting the limitations of the above assumptions, empirical K_d values were calculated for all wells (17) with groundwater and aquifer-solid analyses (Table 3). The 1000 series wells (2) are in a discontinuous glacial-till horizon which overlies the sand and gravel aquifer (i.e., the till is not part of the regional aquifer). Groundwater from well 3016 has been paired with a clay interbed sample that is probably impermeable and, therefore, not interacting with groundwater in the aquifer. These three well numbers have been excluded from discussions which refer to the range and average K_d value. The remaining groundwater-solid pairs (14) have K_d values that range from 0 to 3.89 L/kg, and individual wells had variation in their K_d values from round to round (Table 3). For example, the K_d value calculated for the Round 3 (Fourth Quarter, 1988) groundwater analysis of well 2010 is less than that of the Round 4 (First Quarter, 1989) K_d value because of the larger sulfate value reported for the Round 3 analysis (i.e., less FeOOH sites available for uranium species in Round 3 groundwater).

Empirical K_d values are dependent on the amount of leachable iron (i.e., FeOOH) present in the aquifer solids, the concentration and speciation of uranium in the groundwater, and the

aqueous concentrations of remaining ligands. In general, all anionic complexes except uranium being fixed, the uranium K_d value will:

- Double if the leachable iron in the aquifer solids is doubled, while holding the uranium concentration constant
- Double if the uranium concentration in solution is doubled, while holding leachable iron constant
- Decrease by half if the leachable iron in the aquifer solids is decreased by half, with uranium concentration held constant
- Decrease by half if the uranium concentration in solution decreases by half, with leachable iron held constant
- Decrease by half to zero if all uranium is partitioned into UO₂(CO₃)₂⁻² or UO₂(H₂PO₄)₂*, respectively, while leachable iron is held constant.

Points three and five merit special emphasis because of their sensitivity to the assumptions used in calculating the K_d values. As noted above, iron leached from the aquifer solids can be derived from amorphous- and crystalline-oxyhydroxide grains, and organic complexes. Unfortunately, there is no quantitative way to separate these components and refine the amount of Fe that is partitioned solely into amorphous ferric oxyhydroxide. Therefore, the empirically calculated K_d values overestimate the 'true' K_d value.

Point five is important because speciation modeling predicts most wells to have phosphate concentrations in excess of that required to complex uranium as $UO_2(H_2PO_4)_2^*$ (see Section 3.3). Table 3 reports the K_d value for the empirical model based on the available speciation results for a limited number of groundwaters. Note that K_d values approach zero for those wells which partition greater than 99 percent of the uranium into the neutral phosphate complex (e.g.,1082, 2046, 2095). Based on the present modeling results for uranium speciation, the groundwater-aquifer-solid pairs in Table 3 that were not modeled for speciation would probably have K_d values close to zero, because the phosphate and uranium concentrations suggest most uranium will be partitioned into the neutral phosphate complex. However, for reasons discussed in Section 3.3.1, it is unlikely that the neutral phosphate complex plays as significant a role as predicted by the EQ3NR geochemical code and, if present, this complex would still exhibit some sorptive capacity due to dipole attractions. Therefore, empirical K_d values based

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on the partitioning of greater than 99 percent of the uranium into $UO_2(H_2PO_4)_2$ * will probably underestimate the 'true' K_d of the aquifer.

4.2 AQUIFER SOLIDS, LEACHATES AND GROUNDWATERS

Analytical results for uranium concentrations in groundwaters, leachates and aquifer solids were used to calculate apparent distribution coefficients for 17 monitoring sites. The following assumptions were used in calculating the apparent K_{d} 's:

- The analyzed groundwater samples were in equilibrium with their respective aquifer solids (i.e., kinetic rates for uranium sorption were faster than solution flow rates through a given volume element)
- All uranium species sorb at the same rate
- The background concentration of uranium in the aquifer solids is 3 mg/kg and in the leachates 0.142 mg/kg
- The adsorbed uranium concentration is equal to the concentration of uranium obtained for the aquifer solid or leachate minus the background concentration of uranium
- The apparent K_d is equal to the sorbed uranium concentration (mg/kg) divided by the groundwater uranium concentration (mg/L).

Apparent distribution coefficients were calculated from reported uranium concentrations for aquifer solids from wells 2046 (U = 16 mg/kg) and 4010 (U = 13.8 mg/kg), and round 4 groundwater analyses from wells 2046 (U = 0.309 mg/L) and 4010 (<0.001 mg/L). These samples were chosen because they bound the range of aqueous uranium concentrations available for groundwater analyses that can be matched to the aquifer solids. Using the uranium values cited above, Kd's for wells 2046 and 4010 are, respectively, 42 and 10,800 L/kg. The K_d for well 4010 was calculated with the uranium detection-limit value of 0.001 mg/L. Utilizing the 2-sigma error range for uranium concentrations in the aquifer solids (12.3 to 19.7 mg/kg and 9.7 to 17.9 mg/kg, respectively), the corresponding range in K_d for the respective wells is 30 to 54 L/kg and 6,700 to 14,900 L/kg. Because of the similar uranium concentrations reported for the unleached aquifer solids, the K_d is primarily a function of the uranium concentration in the groundwater. It is important to reemphasize that the uranium concentrations reported for aquifer solids analyzed by gamma spectrometry are suspect, and K_d calculations using these anomalous results yield partition coefficients that are too great for 33 the aquifer.

Results for total uranium concentrations in the leachate fractions derived from the differential-leaching procedure indicate less than 2.5 ppb of uranium is sorbed on aquifer solids (i.e., K_d = 0). In contrast, a range of 33 to 783 ppb of uranium was reported for leachates derived from aquifer solids which underwent the iron- and manganese-leaching procedure (see Section 2.5.2). Utilizing the above assumptions, and a background uranium concentration in the leachates of 0.142 mg/kg (obtained by averaging the leachate uranium values obtained from samples 7790, 10407, 10460, 10607 and 10696, which have reported uranium concentrations in groundwater of less than 1 ppb), K_d values calculated for 14 aquifer wells (1000 series wells and clay interbed sample are not included) ranged from 0 to 68.2 L/kg (Table 4). About a third of the samples have a K_d value of zero, but most of these are from wells considered to be representative of uranium background levels and do not reflect 'true' K_d values. Three samples have distribution coefficients greater than 10. The samples which produced high K_d values were obtained from the waste-pit region bounding the northwest corner of the Fernald compound, and may indicate that precipitated uranium solids are contributing to the sorption K_d value.

4.3 COMPARISON OF EMPIRICAL AND CALCULATED Kd VALUES

Figure 12 is a plot of the calculated K_d from groundwater and leachate analyses versus the predicted K_d based on the empirical sorption model. Wells in the regional aquifer were broken down into areas adjacent to and within the Feed Material Production Center (FMPC) compound. The areas are identified as the south plume (south of the FMPC), waste pit (northwest of the FMPC), and within the FMPC compound. The 1000-series wells in the glacial till are in the waste-pit area but have been plotted separately because they are not part of the regional aquifer. The plot was constructed with the data in Tables 3 and 4 after averaging multiple K_d values for individual wells and omitting well 3016, which had groundwater matched to an anomalous clay-interbed sample.

Monitoring wells in the regional aquifer, representing the south-plume and waste-pit areas, were identified and plotted separately to construct regression lines for these areas. A slope of one on this plot, and a correlation coefficient (r) near one, would indicate a perfect fit between the calculated and predicted K_d . The regression line for the south-plume data has a slope of 0.87, but a less than ideal r value of 0.65. Data points representing the waste-pit area define a regression line with a slope of 6.44 and a r value of 0.29, indicating a poor fit between the

predicted and calculated K_d values. Wells within the FMPC compound and glacial till lie near the south plume regression line (but have not been used in the calculation of the regression line). The poor fit between predicted and calculated K_d values for aquifer samples from the waste pit may indicate that precipitation of amorphous uranium solids has occurred in those samples with calculated K_d values greater than 30 (e.g., 2007, 2010, 2027). If precipitation and sorption are mechanisms responsible for retardation of uranium in the waste-pit area, the empirical model would not be expected to predict accurately the K_d because it is based only on the sorption of uranium.

The precipitation hypothesis is supported by uranium concentrations in groundwater recovered from waste-pit area wells 1073 and 1082 (0.8 to 4.4 mg/L), and 3010 (0.015 to 0.020 mg/L). These samples were obtained from the glacial till above the aquifer (1073 and 1082) and, within the aquifer, from below (3010) the 2000 series samples with high K_d values. If uranium-rich waters in the glacial till vertically infiltrated to the underlying aquifer, mixing at the till/aquifer interface could have resulted in precipitation of amorphous uranium solids in the 2000-series horizon, thus limiting breakthrough to the 3000-series horizon.

4.4 ESTIMATION OF THE URANIUM Kd FOR THE FERNALD SITE AQUIFER

Results presented in Tables 3 and 4, and Figure 12, indicate that the most reliable indicators of uranium K_d values in the Fernald site aquifer come from well locations in the south-plume area. This conclusion is based on the similarity of K_d estimates derived from two independent methods. Wells in the waste-pit area are not considered in the estimation of the aquifer K_d , because large calculated values for 2000-series wells (Table 4) suggest uranium is also present as amorphous oxide solids. Additionally, calculated K_d values (Table 4), rather than empirical K_d values (Table 3), were used to estimate the site K_d because assumptions based on the former are more valid and defensible.

To derive the estimate of the aquifer K_d , 2000- and 3000-series wells from the south-plume area (Table 4) were averaged (if Round 3 and Round 4 values were reported) to produce a single K_d value for each well. Wells with reported K_d values of zero were not considered because of the inability to estimate a reasonable K_d (i.e., a distribution coefficient is a finite

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number). A simple average of the K_d value for each well was considered to be the best approach, because there is no basis on which to weigh individual wells at this time. After satisfying the preceding criteria, four wells (2016, 2046, 2095 and 3095) were used to estimate the aquifer K_d . The mean K_d value for the four wells is 2.38, with a standard deviation of 1.42.

The mean uranium K_d value can be converted to a retardation factor with the relationship:

$$R_f = 1 + (rho/n) \cdot K_d$$

where:

R_f = retardation factor

rho = density

n = porosity

K_d = distribution coefficient

Using the mean K_d value of 2.38 L/kg (note: a L/kg = ml/g), and typical values for rho (2.6 g/cc; cc = ml) and n (0.25) in the sand and gravel aquifer, the R_f value is 25.8. This retardation factor implies that uranium species present in the groundwater will move 1 meter for every 25.8 meters traversed by the groundwater front. Unfortunately, this retardation value is based on the uranium recovered from the iron and manganese leachates, and the uranium present as 'historical' uranium (if any) is estimated from subtracting an 'estimated' background level from the total. Additionally, recall that the differential-leaching of aquifer solids (6 samples) for uranium recovered less than 2.5 ppb uranium, which suggests the above retardation factor is far too great. Resolving these problems will require additional data on the mineral composition of aquifer solids (i.e., petrographic and x-ray diffraction studies to estimate detrital iron-oxide minerals) and a larger sample-size population for the differential-leaching analysis.

Noting the limitations of the present estimate of the aquifer K_d , it is recommended that the solute-transport model be evaluated using the limits defined by the standard deviation of the mean K_d value. This approach requires two runs of the model at bounding conditions of 0.96

L/kg (estimated lower limit) and 3.80 L/kg (estimated upper limit), and would bracket the majority of K_d values calculated for the site (excluding 2000-series wells in the waste-pit area). The bounding conditions can be cautiously applied to the waste-pit area, noting that additional analytical data is required to evaluate the retardation process occurring in these 2000-series wells. Given the current data base available to work with, this is the recommended application of the estimated K_d value to the solute-transport model.

5.0 CONCLUSIONS

5.1 ISSUE THREE

Subsurface soils and surface waters from Paddy's Run and the storm-water-outfall ditch (Fig. 1) have been sampled and analyzed to evaluate the degree of infiltration of uranium-bearing surface water to the underlying aquifer. Presently, there is no indication of contamination at four of the six soil-sample sites. If uranium-rich waters had infiltrated these soil horizons, the present observation suggests uranium was not attenuated (e.g., the dominant specie in the infiltrating waters may have been $UO_2(H_2PO_4)_2$) and/or uranium that had sorbed (e.g., $UO_2(CO_3)_3$) or precipitated was desorbed or dissolved prior to sampling and analysis of the soils. Both of these scenarios are compatible with the modeling results, which predict the presence of neutral uranyl-phosphate and anionic uranyl-carbonate species in the surface waters (Table 2).

The top ten feet of material at sites S1 (1405) and S2 (1406) have concentrations of uranium that are about twice the level of background values. This observation indicates uranium has been retarded at these sites by sorption or precipitation processes occurring in the soil (site S1) and regional aquifer (site S2). The uranium profiles for these sites (Fig. 3) are compatible with scenarios of no breakthrough to the underlying aquifer (i.e., all uranium is retarded by the soil, site S1) and partial breakthrough to the aquifer (i.e., 'historical' uranium is present in the aquifer, site S2). If the retardation of soluble uranium by the soil and aquifer solids is taking place via a sorption process in the unsaturated zone, modeling results indicate the uranium is in the form of anionic uranyl-carbonate species (Table 2). The presence of sorbed or precipitated uranium at these sites presents the potential for future releases to the underlying aquifer.

5.2 ISSUE FIVE

Partitioning of uranium between aquifer solids and groundwater (see Fig. 9 for well locations) was evaluated to calculate an apparent distribution coefficient (K_d) for uranium in the sand and gravel aquifer. The K_d was evaluated by:

- Modeling the uranium speciation of groundwater using the EQ3NR geochemical code and comparing the speciation output to published K_d studies (i.e., the empirical method)
- Obtaining analyses for total uranium on archived aquifer solids, leachates and groundwaters to calculate a K_d directly.

Empirically derived K_d values for well sites in the regional aquifer ranged from 0 to 3.89 L/kg (Table 3). Distribution coefficients near zero for wells that have greater than 99 percent of their uranium partitioned into $UO_2(H_2PO_4)_2^*$ (e.g., 2046 and 2095, Table 3) are probably too low, and reflect the inability to model organic phosphate complexation and sorption processes that take credit for molecular dipole attraction. Speciation results were not available for all groundwaters evaluated with the K_d model, and $UO_2(CO_3)_3^{-4}$ was assumed to be the specie present. This assumption is supported by:

- Speciation results which indicate UO₂(CO₃)₃⁻⁴ is the dominant specie if phosphate concentrations are below the detection limit of 0.02 mg/L (Table 1)
- Experimental anion-exchange tests that recovered greater than 90 percent of the uranium from site groundwater samples (Khan, 1989; personal communication)
- Documented experimental studies that indicate the dominant uranyl ion in bicarbonate solutions at neutral and slightly alkaline pH is UO₂(CO₃)₃⁻⁴ (Ferri et al., 1981).

Additionally, the empirical K_d values are strongly dependent on the amount of iron that is partitioned into amorphous ferric oxyhydroxide. Because it is not possible to separate the leachable iron into amorphous and crystalline components, all iron was assumed to be partitioned into the amorphous phase. This assumption yields K_d values that overestimate the 'true' K_d of the aquifer.

Distribution coefficients calculated directly from analyses of uranium in aquifer solids, leachates and groundwaters range from 0 to greater than 10,000 L/kg. Calculations of distribution

coefficients based on gamma-spectrometry analysis of uranium in aquifer solids (30 to 14,900 L/kg) are not reliable, and are excluded from interpretations based on the leaching results. The differential-leaching procedure revealed that less than 2.5 ppb of uranium is present as sorbed or amorphous uranium products, which suggests the uranium K_d is zero for these samples. However, the iron- and manganese-leaching technique recovered 33 to 783 ppb of uranium from the aquifer solids, resulting in a range of 0 to 68 L/kg for calculated K_d values (Table 4). A background level was subtracted from the uranium values obtained from the iron and manganese leachate prior to the calculation (adsorbed U = total U - background U), and about a third of the samples had a calculated concentration of adsorbed uranium equal to zero, which resulted in a K_d of zero for that sample. It is important to note that those wells with calculated K_d values of zero are mainly from 3000 and 4000 series horizons, which in general show no indication of uranium contamination.

5.2.1 Best Estimate of the Uranium K_d for the Aquifer

The best estimate of the uranium K_d value for the aquifer was derived from calculated K_d values for south-plume wells. Empirical K_d values were not used because the assumptions supporting the derivation are not as valid and defensible as the calculated K_d assumptions. Calculated K_d values for waste-pit area wells were also excluded from the estimate of the site K_d , because 2000-series wells in this area have apparent K_d values that are anomalously high with respect to values calculated for the majority of wells (Fig. 12). These anomalous values may indicate uranium is being retarded by sorption and precipitation processes in the waste-pit area.

Using the calculated K_d values from four south-plume wells (2016, 2046, 2095 and 3095; Table 4), the aquifer K_d was estimated as 2.38 L/kg. This K_d indicates the retardation factor for uranium in the aquifer will be close to 26, which appears to be too great as evidenced by the differential-leaching tests. However, it is recommended that the solute-transport model be evaluated at the lower (0.96 L/kg) and upper (3.80 L/kg) standard-deviation limits. These two bounding cases would bracket the majority of K_d values calculated for the south-plume and waste-pit area wells (excluding the 2000-series waste-pit wells). The bounding cases may be cautiously applied to the waste-pit area, but additional analytical work on aquifer solids is

required to evaluate critically how the mechanisms of sorption and precipitation retard uranium in 2000-series wells from this area.

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TABLE 1

RESULTS FOR URANIUM SPECIATION IN WATERS RECOVERED FROM FERNALD MONITORING WELLS

WELL#	ROUND	рН	Eh mV	U mg/L	P mg/L	SPECIES	%	CB ^a
1019	3	7	386b	0.818	0.061	UO ₂ (CO ₃)3 ⁻⁴ UO ₂ (H ₂ PO ₄)2 ⁰ UO ₂ (CO ₃)2 ⁻²	52 29 19	+14.84 ^C
1019	4	7	371 ^b	0.739	0.12	UO ₂ (H ₂ PO ₄) ₂ ° UO ₂ (CO ₃) ₃ -4 UO ₂ (CO ₃) ₂ -2	62 26 12	+ 7.99
1073	3	7.6	321 ^b	3.297	0.493	UO ₂ (H ₂ PO ₄) ₂ o UO ₂ (CO ₃) ₃ -4 UO ₂ (CO ₃) ₂ -2	57 39 3	+ 2.60
1073	4	7.1	366 ^b	4.38	NR	$UO_2(CO_3)_3^{-4}$ $UO_2(CO_3)_2^{-2}$	92 8	+64.16 ^e
1082	3	7	350 ^f	1.079	3.79	UO ₂ (H ₂ PO ₄) ₂ o	>99	-26.859
1082	4	7.35	350 ^f	0.81	0.65	UO ₂ (H ₂ PO ₄)2 ⁰	>99	+19.61 ^h
2013	3	6.85	137 ⁱ	0.008	<0.02	UO ₂ (CO ₃)2 ⁻² UO ₂ (CO ₃)3 ⁻⁴ UO ₂ (CO ₃)8	67 31 2	+ 4.55
2024	3	7.30	152 ⁱ	0.005	0.342	UO ₂ (H ₂ PO ₄) ₂ o	>99	- 9.46
2044	3	7.47	331	0.033	0.024	UO ₂ (H ₂ PO ₄) ₂ o	>99	- 9.82
2045	4	7.3	324 ^k	0.283	NR	UO ₂ (CO ₃) ₃ -4 UO ₂ (CO ₃) ₂ -2	59 41	+ 5.79
2046	4	7.0	324 ^k	0.309	0.39	UO ₂ (H ₂ PO ₄)2 ⁰	>99	+ 8.68
2060	3	7.50	605 ^l	0.171	<0.02	UO ₂ (CO ₃)3 ⁻⁴ UO ₂ (CO ₃)2 ⁻²	61 39	+ 4.07
2060	4	7.4	324 ^k	0.250	0.03	UO ₂ (H ₂ PO ₄) ₂ ° UO ₂ (CO ₃)3 ⁻⁴ UO ₂ (CO ₃)2 ⁻²	45 32 23	+ 3.74
2061	4	7.6	₃₂₄ b	0.292	0.02	UO ₂ (CO ₃)3 ⁻⁴ UO ₂ (H ₂ PO ₄)2 ⁰ UO ₂ (CO ₃)2 ⁻²	50 25 24	+ 4.87
2094	4	7.1	75 ⁱ	0.0045	1.92	UO ₂ (H ₂ PO ₄) ₂ o	>99	+54.91 ^m
2095	3	7.33	331 ^j	0.177	0.063	UO ₂ (H ₂ PO ₄) ₂ o	>99	+14.65 ⁿ

TABLE 1 RESULTS FOR URANIUM SPECIATION IN WATERS RECOVERED FROM FERNALD MONITORING WELLS (CONTINUED)

WELL #	ROUND	рН	Eh mV	U mg/L	P mg/L	SPECIES	%	CB ^a
3001	3	8	810	0.015	<0.02	UO ₂ (CO ₃) ₃ -4 UO ₂ (CO ₃) ₂ -2	89 11	+20.52 ^p
3001	4	7.1	81 ⁱ	0.015	0.12	UO ₂ (H ₂ PO ₄) ₂ o	>99	+ 6.00
3013	3	6.30	139 ⁰	0.011	<0.02	UO ₂ (CO ₃)2 ⁻² UO ₂ (CO ₃)3 ⁻⁴ UO ₂ (CO ₃)8	77 19 4	+ 4.83
3013	4	8.4	139 ⁱ	0.49	0.02	UO ₂ (CO ₃)3 ⁻⁴ UO ₂ (H ₂ PO ₄) ₂ ° UO ₂ (CO ₃)2 ⁻²	79 15 6	+ 1.22
3014	3	7.75	575 ^l	0.028	<0.02	$UO_2(CO_3)_3^{-4}$ $UO_2(CO_3)_2^{-2}$	70 30	+ 1.56
3016	3	7.60	331 ^j	0.008	<0.05	$UO_2(CO_3)_3^{-4}$ $UO_2(CO_3)_2^{-2}$	64 35	-15.249
3062	3	7.90	331 ^b	0.041	<0.02	$UO_2(CO_3)_3^{-4}$ $UO_2(CO_3)_2^{-2}$	83 17	+ 6.59
3069	3	7.60	331 ^j	0.005	0.662	UO ₂ (H ₂ PO ₄) ₂ °	>99	- 5.92
3094	4	7.1	99 ⁱ	0.0006	0.88	UO ₂ (H ₂ PO ₄) ₂ °	>99	+58.57 ^m
4097	4	7.1	221 ⁱ	0.0019	0.11	UO ₂ (H ₂ PO ₄) ₂ °	>99	+ 1.77

NR = no analysis reported.

^bEh estimated from the NH₄+/NO₃ redox couple.

dominant aqueous Th-specie (>99 %) is Th(OH)4.

Platinum-electrode measurement.

ⁿExcessive charge balance probably due to low CI concentrartion (4 mg/L).

^oEh value obtained from round 4 analysis of same well number.

^aCharge balance expressed as percent of total charge.

CExcessive charge balance probably due to high Mg or Na concentrations (159 and 437 mg/L, respectively). ^dEQ3NR calculations indicate the groundwater sample is supersaturated with respect to thorianite, and the

^eExcessive charge balance probably results from high Ca concentration (4000 mg/L). ^fEh estimated from results of NH₄⁺/NO₃⁻ redox couple in wells 1019 and 1073. ^gExcessive charge balance probably due to high SO₄⁻² concentration (510 mg/L). ^hExcessive charge balance probably due to low SO₄⁻² concentration (19.6 mg/L).

Eh value estimated from NH₄⁺/NO₃ redox couple for well 3062. Eh value estimated from NH₄⁺/NO₃ redox couple for well 2061. Eh based on pyrolusite saturation.

mExcessive charge balance probably results from high K concentration (1800-1830 mg/L).

PExcessive charge balance probably due to high Ca and Na concentrations (173 and 24.4 mg/L, respectively), relative to round 4 analysis of same well.

^qExcessive charge balance probably due to high SO₄-2 concentration (174 mg/L).

TABLE 2

RESULTS FOR URANIUM SPECIATION IN SURFACE WATERS RECOVERED FROM PADDY'S RUN, FERNALD SITE

SAMPLE #	рН	Eh	Р	U	SPECIES	%	CBa
		mV	mg/L				
W-07	8.38	451	0.032	0.015	UO ₂ (H ₂ PO ₄) ₂ o	>99	+2.99
W-11	8.58	441	BDL	0.009	$UO_2(CO_3)_3^{-4}$ $UO_2(CO_3)_2^{-2}$	90 10	+3.36
ASIT003	8.57	452	0.161	0.002	UO ₂ (H ₂ PO ₄) ₂ 0	>99	+1.99

BDL = below detection limit

^aCharge balance expressed as percent of total charge.

TABLE 3 EMPIRICAL URANIUM DISTRIBUTION COEFFICIENTS FOR SELECTED MONITORING WELLS

WELL	GW ^a	HCO3 ⁻ mg/L	NO3 ⁻ mg/L	HPO ₄ -2 mg/L	SO ₄ -2 mg/L	U mg/L	ASb	Fe ^c mg/g	K _d ^d L∕kg	K _d e L∕kg
REGION	NAL AQUIFE	R								
	lume Area									
2016	rd1 ^f	292	<22	0.87	59	0.021	10437	0.69	2.27	NAg
2046	3997	355	5.98	1.21	74	0.309	8956	0.81	2.15	0.02
2095	3787	352	77.5	0.20	18	0.177	10038	0.66	1.77	0.02
2095	397.6	349	13.1	2.7	137	0.146	10038	0.66	1.48	NAG
3095	3786	370	<0.4	0.409	18	0.005	10049	1.00	3.08	NA9
3095	3971	335	<0.4	2.98	90	0.006	10049	1.00	2.67	NAg
4014	rd4 ^f	285	<0.4	NRh	58	<0.001	10407	1.08	0.00	NA9
4016	rd4 ^f	313	<0.4	NRh	98	<0.001	10460	0.38	0.00	NAG
Waste-F	Pit Area									
2007	rd5 ^f	311	<0.4	4.25	123	0.005	10796	1.08	2.76	PAN
2010	3715	368	<0.4	0.17	271	0.005	8426	1.50	2.55	NAG
2010	3902	382	<0.08	8.1	140	0.021	8426	1.50	3.18	NVa
2027	3941	406	<0.08	0.06	245	0.007	7874	1.58	2.67	2.45
2034	3646	287	9.74	0.136	39	0.024	8286	0.78	2.73	2.51
3010	3714	428	12.3	< 0.06	712	0.020	10611	3.50	3.15	NAG
3010	3901	426	0.84	0.06	520	0.015	10611	3.50	3.89	NAG
4010	rd4 ^f	399	<0.08	0.25	36	<0.001	10607	1.08	0.00	NA9
FMPC C	Compound									
2013	3709	328	<0.4	<0.06	97	0.008	10670	0.65	1.74	1.12
2013	3900	311	0.13	0.37	110	0.036	10670	0.65	1.74	PAN PAN
2054	rd5 ^f	402	<0.4	0.82	666	0.023	8645	1.17	1.13	NAG
Clay Into	erbed									
3016	rd1 ^f	270.2	0.4	<0.15	56	0.011	10449	4.83	17.1	13.9
3016	rd4 ^f	242.8	11.6	0.22	60	0.007	10449	4.83	17.7	NAG
GLACIA										
Waste-F										
1073	3775	481	420	1.53	612	3.297	8561	1.00	0.72	0.29
1073	3951	455	872	NR ^h	428	4.380	8561	1.00	0.65	0.62
1082	3765	531	<0.4	11.75	510	1.079	7667	0.81	0.82	0.01
1082	3949	518	<0.4	2.01	20	0.810	7667	0.81	1.80	0.02

aGroundwater sample ID
bAquifer-solid sample ID
CLeachable iron obtained from aquifer solid
dDistribution coefficient based on all U partitioned into UO₂(CO₃)₃-4
eDistribution coefficient based on speciation in Table 1
fRound number indicated because sample ID not available
gSpeciation results not available
hAnalysis not reported

TABLE 4 CALCULATED URANIUM DISTRIBUTION COEFFICIENTS FOR SELECTED MONITORING WELLS

WELL	GW ^a	U mg/L	AQ ^b	U mg/kg	U _{ads} c mg/kg	K _d ^d L/kg
REGIONAL AC	UIFER				•	
South-Plume A	rea					
2016	rd1 ^e	0.021	10437	0.158	0.016	0.76
2046	3997	0.309	8956	0.675	0.533	1.72
2095	3787	0.177	10038	0.783	0.641	3.62
2095	3976	0.146	10038	0.783	0.641	4.39
3095	3786	0.005	10049	0.158	0.016	3.20
3095	3971	0.006	10049	0.158	0.016	2.67
4014	rd4 ^e	<0.001	10407	0.117	0	0
4016	rd4 ^e	<0.001	10460	0.033	0	0
Waste-Pit Area						
2007	rd5 ^e	0.005	10796	0.483	0.341	68.2
2010	3715	0.005	8426	0.408	0.266	53.2
2010	3902	0.021	8426	0.408	0.266	12.7
2027	3941	0.007	7874	0.383	0.241	34.4
2034	3646	0.024	8286	0.117	0	0
3010	3714	0.020	10611	0.183	0.041	2.05
3010	3901	0.015	10611	0.183	0.041	2.73
4010	rd4 ^e	<0.001	10607	0.217	0.075	0
FMPC Compou	ind					
2013	3709	0.008	10670	0.092	0	0
2013	3900	0.036	10670	0.092	0	0
2054	rd5 ^e	0.023	8645	0.333	0.191	8.3
Clay Interbed						
3016	rd1 ^e	0.011	10449	0.133	0	0
3016	rd4 ^e	0.007	10449	0.133	. 0	0
GLACIAL TILL						
Waste-Pit Area						
1073	3775	3.297	8561	0.675	0.533	0.16
1073	3951	4.38	8561	0.675	0.533	0.12
1082	3765	1.079	7667	0.367	0.225	0.21
1082	3949	0.81	7667	0.367	0.225	0.28

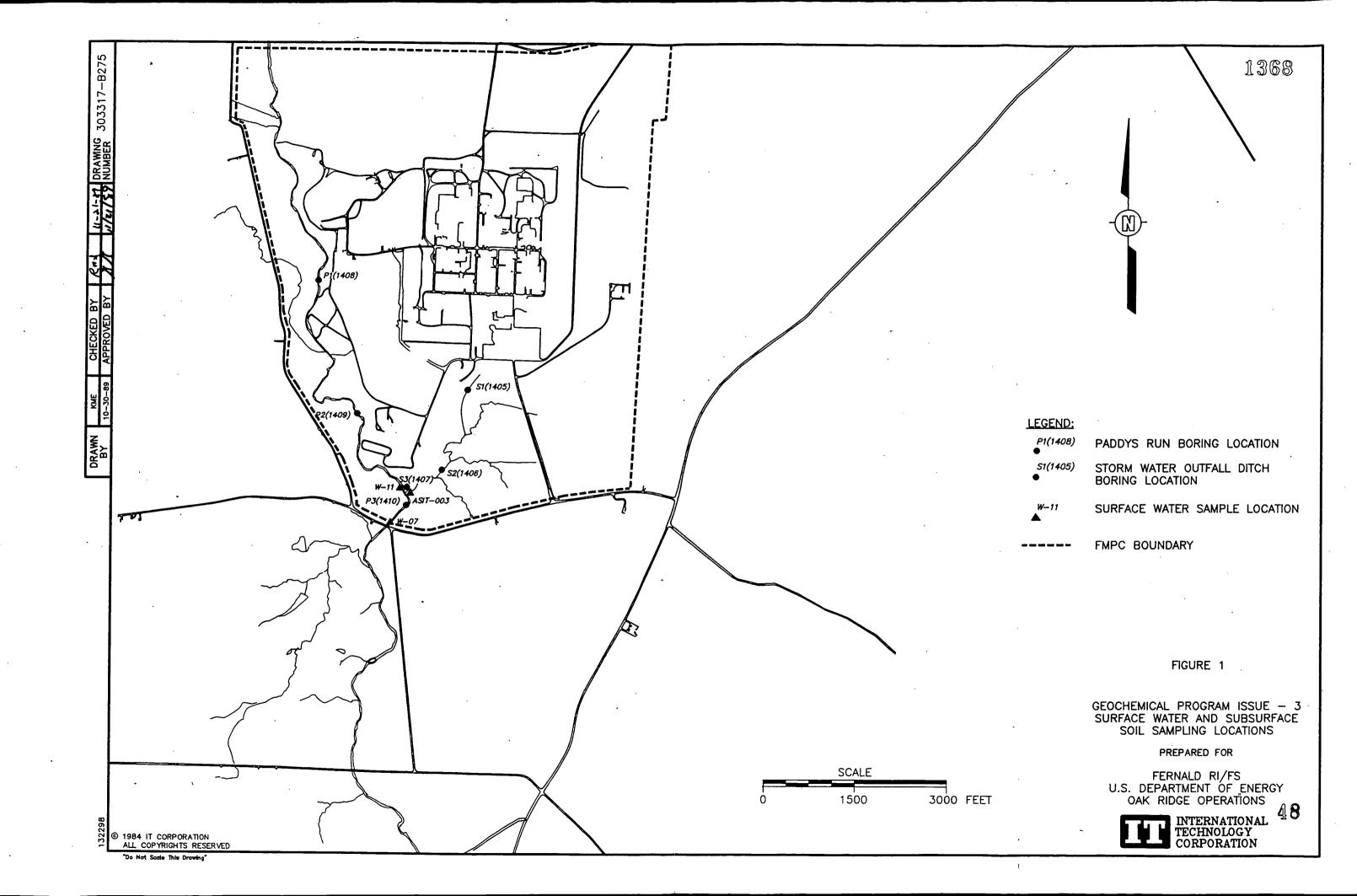
^aGroundwater sample number

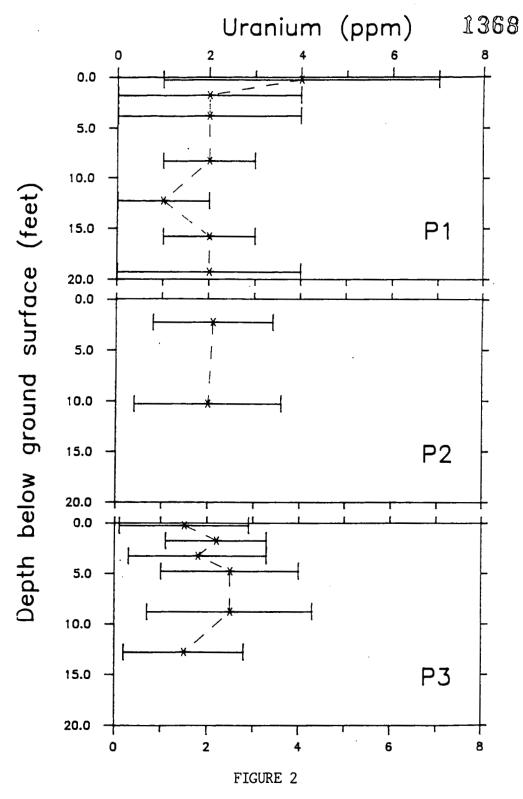
Aquifer-solid sample number

CAdsorbed uranium (total uranium - background of 0.142)

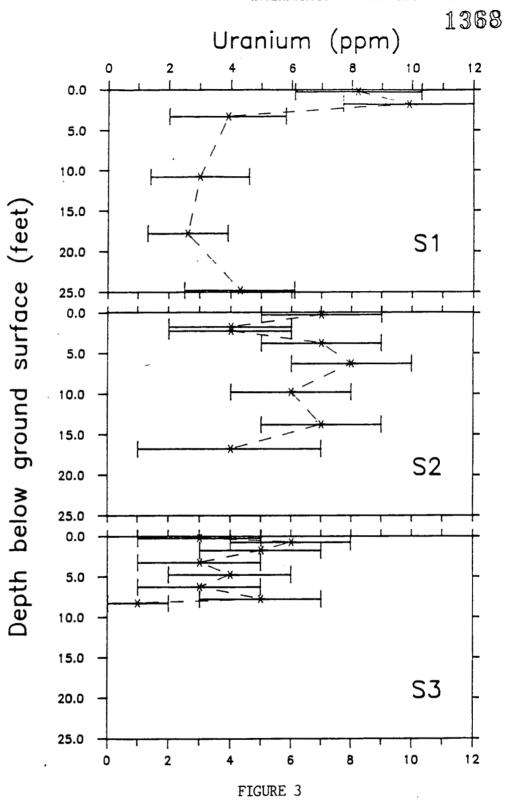
Distribution coefficient calculated from adsorbed uranium and groundwater uranium values

Round number indicated because sample ID not available

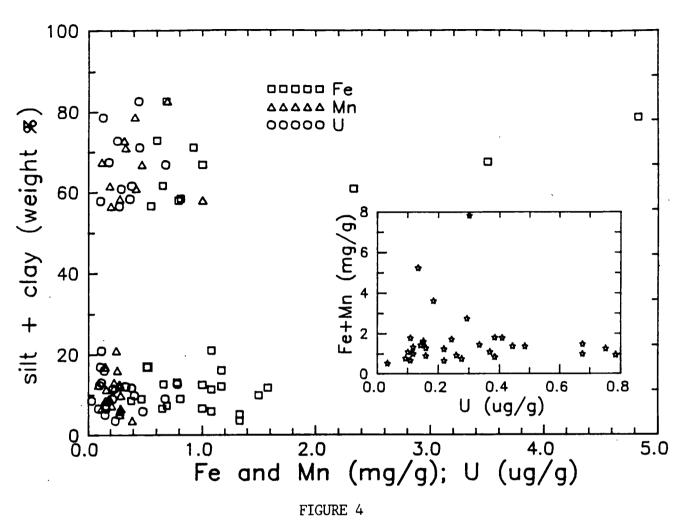




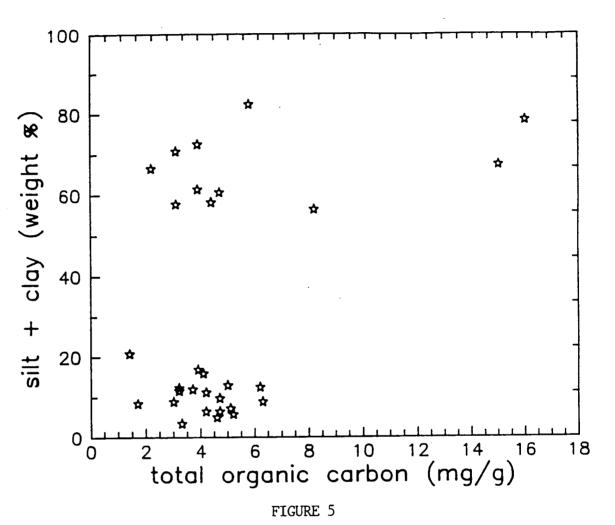
URANIUM CONCENTRATIONS IN SUBSURFACE SOILS OF PADDY'S RUN



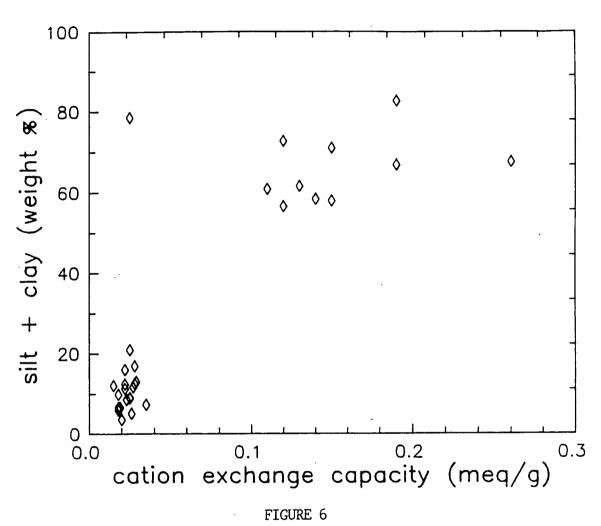
URANIUM CONCENTRATIONS IN SUBSURFACE SOILS OF THE STORM-WATER-OUTFALL DITCH



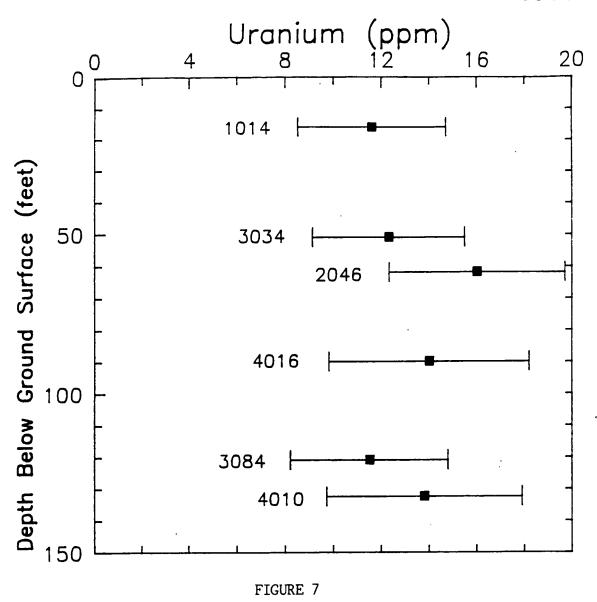
WEIGHT PERCENT OF SILT + CLAY VERSUS LEACHABLE IRON, MANGANESE AND URANIUM



WEIGHT PERCENT OF SILT + CLAY VERSUS TOTAL ORGANIC CARBON

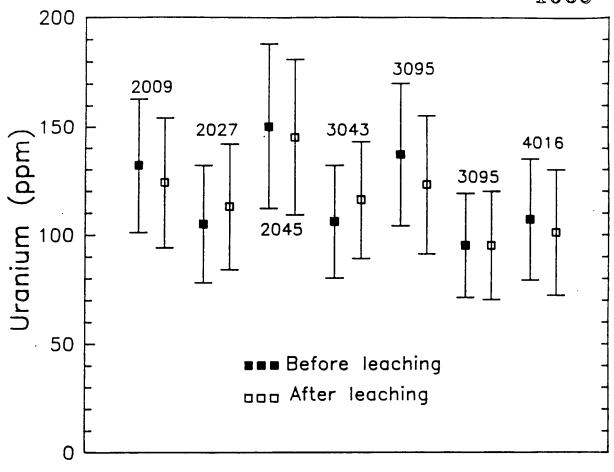


WEIGHT PERCENT OF SILT + CLAY VERSUS CATION EXCHANGE CAPACITY



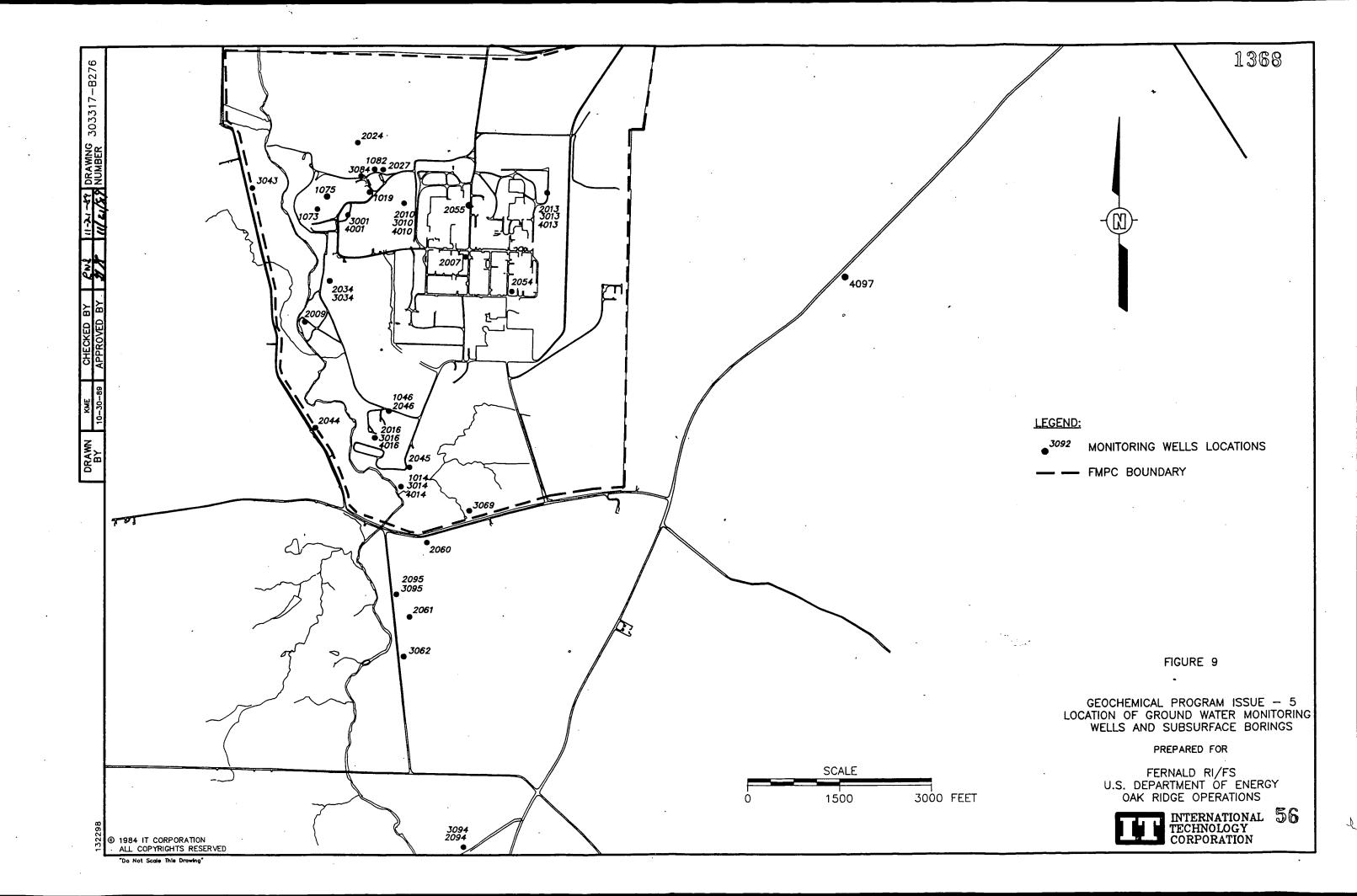
URANIUM CONCENTRATIONS IN AQUIFER SOLIDS

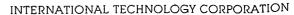




RESULTS OF THE URANIUM DIFFERENTIAL-LEACH TEST

FIGURE 8





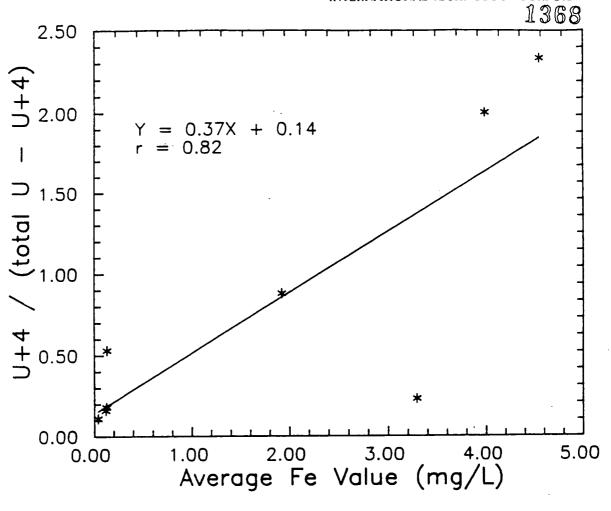
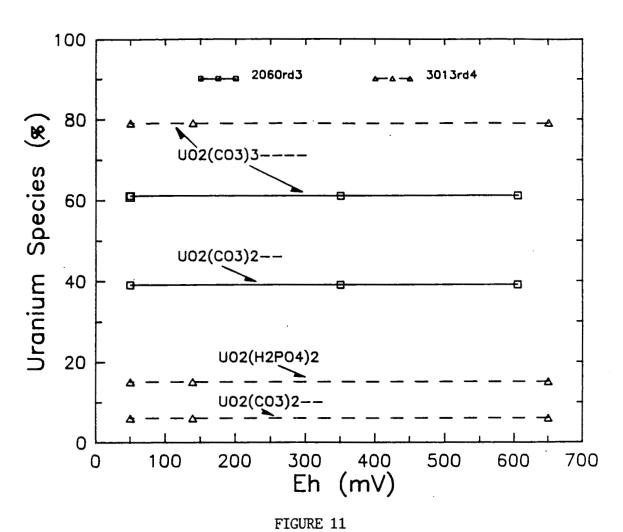
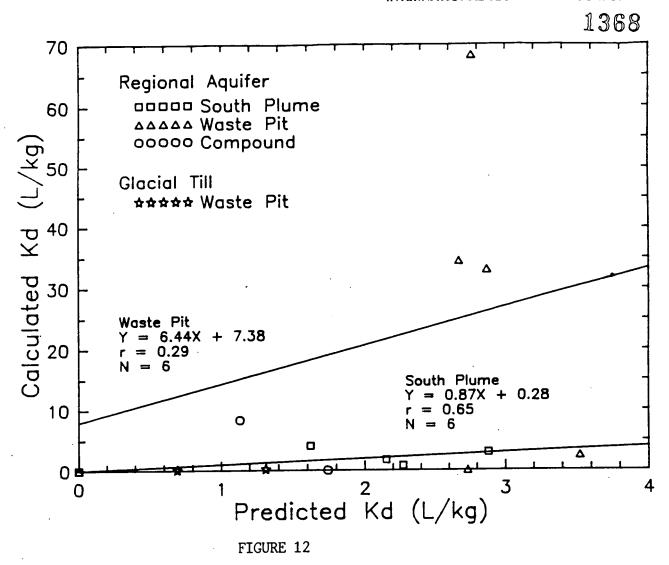


FIGURE 10

URANIUM REDOX RATIO VERSUS TOTAL IRON



URANIUM SPECIATION AS A FUNCTION OF THE GROUNDWATER Eh



CALCULATED Kd VERSUS PREDICTED Kd

APPENDIX A ANALYTICAL RESULTS

APPENDIX A ANALYTICAL RESULTS FOR SOIL SAMPLES

· · · · · · · · · · · · · · · · · · ·					
SITE # Sample ID Sample Date Sample Depth (ft)	P1 98152 06/02/89 0.0- 0.5	P1 98153 06/02/89 1.5- 2.0	P1 98155 06/02/89 3.5- 4.0	P1 98162 06/02/89 8.0- 8.5	P1 98168 06/02/89 12.0- 12.5
U-total (ug/g) 2-sigma error	3	2 2	2 2	2	1 1
SITE # Sample ID Sample Date Sample Depth (ft)	P1 98174 06/02/89 15.5- 16.0	P1 98180 06/02/89 19.0- 19.5	P1 98189 06/02/89 23.5- 24.0	P2 98116 05/31/89 0.0- 0.5	P2 98117 05/31/89 1.5- 2.0
U-total (ug/g) 2-sigma error	2	2	<2	<2	<3
SITE # Sample ID Sample Date Sample Depth (ft)	P2 98118 05/31/89 2.0- 2.5	P2 98119 05/31/89 3.0- 3.5	P2 98125 05/31/89 6.5- 7.0	P2 98132 05/31/89 10.0- 10.5	P2 98143 05/31/89 15.5- 16.0
U-total (ug/g) 2-sigma error	2.1 1.3	<3.5	<3.0	2.0 1.6	<2.5
SITE # Sample ID Sample Date Sample Depth (ft)	P2 98151 05/31/89 19.5- 20.0	P3 98029 05/16/89 0.0- 0.5	P3 98030 05/16/89 1.5- 2.0	P3 98032 05/16/89 3.0- 3.5	P3 98034 05/16/89 4.5- 5.0
U-total (ug/g) 2-sigma error	<3.4	1.5 1.4	2.2 1.1	1.8 1.5	2.5 1.5
SITE # Sample ID Sample Date Sample Depth (ft)	P3 98040 05/22/89 8.5- 9.0	P3 98047 05/22/89 12.5- 13.0	P3 98054 05/22/89 16.0- 16.5	P3 98061 05/22/89 19.5- 20.0	
U-total (ug/g) 2-sigma error	2.5 1.8	1.5 1.3	<2.9	<2.8	

APPENDIX A ANALYTICAL RESULTS FOR SOIL SAMPLES

SITE # Sample ID Sample Date Sample Depth (ft)	S1	S1	S1	S1	S1
	98062	98064	98066	98077	98089
	05/24/89	05/24/89	05/24/89	05/24/89	05/24/89
	0.0-	1.5-	3.0-	10.5-	17.5-
	0.5	2.0	3.5	11.0	18.0
U-total (ug/g)	8.2	9.9	3.9	3.0	2.6
2-sigma error	2.1	2.2	1.9	1.6	1.3
SITE # Sample ID Sample Date Sample Depth (ft)	S1	S1	S1	S2	S2
	98100	98106	98115	98010	98011
	05/24/89	05/24/89	05/24/89	05/16/89	05/16/89
	24.5-	28.5-	33.5-	0.0-	1.5-
	25.0	29.0	34.0	0.5	2.0
U-total (ug/g)	4.3	<3.0	2.7	7	4
2-sigma error	1.8		1.3	2	2
SITE # Sample ID Sample Date Sample Depth (ft)	S2	S2	S2	S2	S2
	98012	98014	98017	98020	98024
	05/16/89	05/16/89	05/16/89	05/16/89	05/16/89
	2.0-	3.5-	6.0-	9.5-	13.5-
	2.5	4.0	6.5	10.0	14.0
U-total (ug/g)	4	7	8	6	7
2-sigma error	2	2	2	2	2
SITE # Sample ID Sample Date Sample Depth (ft)	S2 98028 05/16/89 16.5- 17.0	\$3 98000 05/16/89 0.0- 0.5	S3 98001 05/16/89 0.5- 1.0	S3 98002 05/16/89 1.5- 2.0	S3 98003 05/16/89 3.0- 3.5
U-total (ug/g)	4 3	3	6	5	3
2-sigma error		2	2	2	2
SITE # Sample ID Sample Date Sample Depth (ft)	S3 98004 05/16/89 4.5- 5.0	S3 98006 05/16/89 6.0- 6.5	S3 98008 05/16/89 7.5- 8.0	S3 98009 05/16/89 8.0- 8.5	
U-total (ug/g) 2-sigma error	4 2	3 2	5 2	1	

APPENDIX A
ANALYTICAL RESULTS FOR SURFACE WATERS

Sample ID	ASIT003	W-07	W-11	
Sample Date	05/14/89	05/14/89	05/14/89	
pН	8.57	8.38	8.58	
Eh (mV)	452	451	441	
O ₂ (mg/L)	8.6	10.2	11.8	
T (°C)	15.5	13	18	
. ()	, 5.0			
CI (mg/L)	34	18.19	19.99	
F (mg/L)	0.19	0.21	0.18	
HCO ₃ (mg/L)	200.5	256.5	212	
NH ₄ ⁺ (mg/L)	0.162	<0.1 ^a	<0.1	
NO_3^- (mg/L)	24.08	11.95	10.23	
P (mg/L)	0.161	0.032	<0.02	
SO_4^{-2} (mg/L)	51.3	57.36	57.36	
Ag (mg/L)	<0.01	<0.01	<0.01	
Al (mg/L)	0.0866	<0.06	0.0764	
As (mg/L)	< 0.002	< 0.002	<0.002	
Ba (mg/L)	0.0399	0.0374	0.0313	
Ca (mg/L)	72.3	84.7	71.8	
Cd (mg/L)	< 0.002	< 0.002	<0.002	
Cr (mg/L)	<0.01	<0.01	<0.01	
Cu (mg/L)	<0.01	<0.01	<0.01	
Fe (mg/L)	0.0659	0.0286	0.0415	
Hg (mg/L)	<0.0002	0.0002	0.0003	
K (mg/L)	1.84	1.55	1.68	
Mg (mg/L)	19.9	21.4	20.9	
Mn (mg/L)	0.0097	0.0152	0.0121	
Mo (mg/L)	<0.01	<0.01	<0.01	
Na (mg/L)	14.6	9.93	9.69	
Ni (mg/L)	<0.02	<0.02	<0.02	
Pb (mg/L)	0.0026	0.0093	0.0074	
Se (mg/L)	<0.002	< 0.002	<0.002	
Si (mg/L)	3.89	1.73	2.25	
Th (mg/L)	< 0.006	< 0.002	<0.006	
U (mg/L)	0.002	0.015	0.009	
V (mg/L)	<0.01	<0.01	<0.01	

^aLess than sign indicates value is below detection limit.

APPENDIX A ANALYTICAL RESULTS FOR AQUIFER SOLIDS

WELL#	1014	1046	1073	1075	1082	
Sample ID	07363	08016	08561	08572	07667	
Sample Depth (ft)	15.0-	3.0-	18.0-	21.0-	13.5-	
	16.5	4.5	19.5	22.5	15.0	
Leached Metals ^a						
Fe (mg/g)	1.33	0.68	1.00	0.92	0.81	
Mn (mg/g)	0.28	0.69	0.47	0.33	0.28	
U-total (ug/g)	0.150	0.442	0.675	0.750	0.367	
2-sigma error	0.017	0.050	0.067	0.083	0.042	
TOC ^b (mg/g)	4.6	5.8	2.2	3.1	4.4	
CEC ^C (meq/g)	0.026	0.190	0.190	0.150	0.140	
<200 mesh ^d (wt %)	5.03	82.50	66.63	70.90	58.24	
, , , , , ,				, 0.00		
U-total (ug/g)	11.6	NA ^e	NA	NA	NA	
2-sigma error	3.1					
WELL#	2007	0007	0000	0010	0007	_
Sample ID	10779	2007 10796	2009 07084	2010	2027	
Sample Depth (ft)	10779 13.5-	65.0-	38.5-	08426 70.0-	07874	
Cample Depth (It)	15.0	66.5	36.5- 40.0	70.0- 71.5	65.0- 66.5	
	13.0	00.5	40.0	71.5	66.5	
Leached Metals						
Fe (mg/g)	2.33	1.08	0.52	1.50	1.58	
Mn (mg/g)	0.42	0.28	0.15	0.29	0.23	
U-total (ug/g)	0.292	0.483	0.108	0.408	0.383	
2-sigma error	0.033	0.058	0.017	0.042	0.042	
TOO ())						
TOC (mg/g)	4.7	5.2	3.9	4.7	3.2	
CEC (meq/g)	0.110	0.018	0.028	0.018	0.027	
<200 mesh (wt %)	60.74	5.83	16.85	9.79	11.63	
U-initial ^f (ug/g)	NA	NA	132	NA	105	
2-sigma error			31	• • •	27	
U-final ⁹ (ug/g)	NA	NA	124	NA	113	
2-sigma error		•	30		29	
						_

^aSample leached with a solution of acetic acid and hydroxylamine hydrochloride ^bTOC = total organic carbon

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CEC = cation exchange capacity

dWeight percent of sample less than 0.075 mm (silt + clay)

eAnalysis not available

fTotal uranium before differential-leaching analysis

gTotal uranium after differential-leaching analysis

APPENDIX A ANALYTICAL RESULTS FOR AQUIFER SOLIDS

WELL#	2045	2046	2054	2054	2054
Sample ID	08947	08956	10414	10416	08645
Sample Depth (ft)	30.0-	61.0-	6.0-	9.0-	70.0-
	31.5	62.5	7.5	10.5	71.5
Leached Metals ^a					
Fe (mg/g)	0.47	0.81	0.55	0.65	1.17
Mn (mg/g)	0.19	0.18	0.20	0.19	0.28
U-total (ug/g)	0.217	0.675	0.275	0.383	0.333
2-sigma error	0.025	0.075	0.025	0.042	0.033
_					
TOC ^b (mg/g)	3.0	, 6.3	8.2	3.9	3.7
CEC ^C (meq/g)	0.025	0.025	0.120	0.130	0.015
<200 mesh ^d (wt %)	8.92	8.92	56.44	61.46	11.98
II total /ug/g)	NA ^e	16	NA	NA	NA
U-total (ug/g) 2-sigma error	INA	3.7	11124	INA	IVA
U-initial ^f (ug/g)	150	NA	NA	NA	NA
2-sigma error	38	IVA	INA	INA	IVA
U-final ⁹ (ug/g)	145	NA	NA	NA	NA
2-sigma error	36	INA	IVA	NA.	11/4
2-sigma error					
WELL#	2055	2055	3034	3043	3043
Sample ID	10736	10766	08286	07619	07790
Sample Depth (ft)	1.5-	70.0-	50.0-	7.5-	108.0-
	3.0	71.5	51.5	9.0	109.5
Locabad Motale					
Leached Metals Fe (mg/g)	0.79	1.17	0.78	0.60	1.00
Mn (mg/g)	1.00	0.26	0.78	0.32	0.09
U-total (ug/g)	0.108	0.28 0.142	0.23 0.117	0.258	0.100
2-sigma error	0.108	0.142	0.017	0.233	0.008
2-signia enoi	0.008	0.017	0.017	0.000	0.000
TOC (mg/g)	3.1	4.1	5.0	3.9	3.2
CEC (meq/g)	0.150	0.022	0.029	0.120	0.022
<200 mesh (wt %)	57.80	15.95	12.96	72.64	12.34
U-total (ug/g)	NA	NA	12.3	NA	NA
2-sigma error	13/7	(NA	3.2	IVA	17/1
U-initial (ug/g)	NA	NA	NA	NA	106
2-sigma error	14/1	11/1	17/7	19/3	26
U-final (ug/g)	NA	NA	NA	NA	116
2-sigma error	14/7	13/3	17/3	14/1	27
E Signia error					

aSample leached with a solution of acetic acid and hydroxylamine hydrochloride bTOC = total organic carbon CCEC = cation exchange capacity dWeight percent of sample less than 0.075 mm (silt + clay) Analysis not available Total uranium before differential-leaching analysis gTotal uranium after differential-leaching analysis

APPENDIX A ANALYTICAL RESULTS FOR AQUIFER SOLIDS

WELL#	3084	3095	3095	4010	4010
Sample ID	07558	10038	10049	10611	10607
Sample Depth (ft)	120.0-	20.0-	75.0-	131.5-	195.0-
	121.5	21.5	76.5	132	196.5
Leached Metalsa					
Fe (mg/g)	7.67	0.66	1.00	3.50	1.08
Mn (mg/g)	0.16	0.28	0.29	0.12	0.16
U-total (ug/g)	0.300	0.783	0.158	0.183	0.216
2-sigma error	0.033	0.083	0.017	0.017	0.025
TOC ^b (mg/g)	3.3	6.2	4.7	15.0	4.2
CEC ^C (meq/g)	0.250	0.028	0.018	0.260	0.022
<200 mesh ^d (wt %)	NAe	12.52	6.52	67.38	11.26
U-total (ug/g)	11.5	NA	NA	13.8	NA
2-sigma error	3.3	1471		4.1	•••
U-initial ^f (ug/g)	NA	137	95	NA NA	NA
2-sigma error	14/1	33	24	1473	1471
U-final ⁹ (ug/g)	NA	123	93	NA	NA
2-sigma error		32	25	1471	
WELL#	4013	4013	4014	4016	4016
Sample ID	10670	10696	10407	10437	10449
Sample Depth (ft)	75.0-	205.0-	135.0-	30.0-	89.3-
,	76.5	206.5	136.5	31.5	89.6
Leached Metals					
Fe (mg/g)	0.65	1.33	1.08	0.69	4.83
Mn (mg/g)	0.12	0.39	0.25	0.21	0.41
U-total (ug/g)	0.092	0.242	0.117	0.158	0.133
2-sigma error	0.008	0.025	0.017	0.017	0.017
TOC (mg/g)	4.2	3.3	1.4	5.1	16.0
CEC (meq/g)	0.019	0.020	0.025	0.035	0.190
<200 mesh (wt %)	6.54	3.50	20.88	7.24	78.50
U-total (ug/g)	NA	NA	NA	NA	14.0
2-sigma error					4.2
U-initial (ug/g)	NA	NA	NA	107	NA
2-sigma error				28	
U-final (ug/g)	NA	NA	NA	101	NA
2-sigma error				29	

aSample leached with a solution of acetic acid and hydroxylamine hydrochloride bTOC = total organic carbon cCEC = cation exchange capacity dWeight percent of sample less than 0.075 mm (silt + clay) eAnalysis not available fTotal uranium before differential-leaching analysis gTotal uranium after differential-leaching analysis

APPENDIX A ANALYTICAL RESULTS FOR AQUIFER SOLIDS

 	the second secon	
WELL#	4016	<u>-</u>
Sample ID	10460	
Sample Depth (ft)	145.0-	
	146.5	
Leached Metals ^a		
Fe (mg/g)	0.38	
Mn (mg/g)	0.15	
U-total (ug/g)	0.033	
2-sigma error	0.008	
TOC ^b (mg/g)	1.7	
CEC ^C (meg/g)	0.023	
CEC ^c (meq/g) <200 mesh ^d (wt %)	8.50	
,		

^aSample leached with a solution of acetic acid and hydroxylamine hydrochloride ^bTOC = total organic carbon ^cCEC = cation exchange capacity ^dWeight percent of sample less than 0.075 mm (silt + clay)

APPENDIX A ANALYTICAL RESULTS FOR MODELED GROUNDWATERS

WELL # Sample ID Sample Date Round #	1019 3748 12/04/88 3	1019 3944 03/08/89 4	1073 3775 12/04/88 3	1073 3951 03/12/89 4	1082 3765 11/20/88 3
pH Eh (mV) O _{2_} (mg/L)	7 NR ^a 10.6	7 NR 2.8	7.6 NR 6.25	7.1 NR 8.1	7 NR 8
T (°C)	11	7	12.5	10.5	13
CI (mg/L)	1160	490	1030	1170	2
F (mg/L)	0.48	0.5	6.25	7.25	1.25
HCO ₃ (mg/L)	403.8	395.8	480.6	454.9	530.8
NH ₄ ^F (mg/L)	0.139	0.5	80.2	71.6	<0.1 ^b
NO ₃ (mg/L)	56.7	0.9	419.7	872	<0.4
P (mg/L) SO ₄ -2 (mg/L)	0.061	0.12	0.493	NR	3.79
SO ₄ -2 (mg/L)	224	250	612	428	510
Ag (mg/L)	<0.02	0.01	<0.02	<0.0005	<0.0005
As (mg/L)	0.004	<0.003	0.002	<0.002	<0.002
Ba (mg/L)	0.195	0.1	0.138	0.126	0.044
Ca (mg/L)	522	300	413	4000	129
Cd (mg/L)	0.002	0.006	0.002	0.0364	<0.002
Cr (mg/L)	<0.02	0.04	<0.02	0.0464	<0.02
Cu (mg/L)	<0.01	<0.01	0.014	0.0836	<0.01
Fe (mg/L)	1.51	0.87	0.073	0.172	0.015
Hg (mg/L)	< 0.0002	<0.0002	0.0007	30.2	<0.0002
K (mg/L)	1.47	0.86	33	0.0007	2.42
Mg (mg/L)	159	86	325	364	65
Mn (mg/L)	1.61	1.1	2.1	0.689	0.008
Mo (mg/L)	<0.02	0.02	0.533	0.58	0.033
Na (mg/L)	437	170	149	178	13.3
Ni (mg/L) Pb (mg/L)	<0.02 0.003	<0.03 <0.002	0.066 0.004	0.114 <0.002	<0.02 <0.002
Se (mg/L)	<0.003	<0.002 <0.005	<0.004	<0.002	0.002
Th (mg/L)	<0.002	<0.005 <0.005	0.002	0.025	<0.002
U (mg/L)	0.818	0.739	3.297	4.38	1.079
<u> </u>	0.010	U./ 35	J.231	7.50	1.0/3

^aNR = analysis not reported bLess than sign indicates below detection limit value

APPENDIX A ANALYTICAL REUSULTS FOR MODELED GROUNDWATERS

WELL #	1082	2013	2024	2044	2045
Sample ID	3949	3709	3656	3682	3993
Sample Date	02/05/89	11/15/88	11/02/88	11/03/88	01/23/89
Round #	4	3	3	3	4
pH	7.35	6.85	7.30	7.47	7.3
Eh (mV)	NR ^a	NR	152	NR	NR
O ₂ (mg/L)	8	1.3	0.4	4.39	3.6
T (^O C)	10	13	10	10	7
CI (mg/L) F (mg/L) HCO3 ⁻ (mg/L) NH4 ⁺ (mg/L) NO3 ⁻ (mg/L) P (mg/L) SO4 ⁻² (mg/L) Ag (mg/L) As (mg/L) Ca (mg/L) Cd (mg/L) Cr (mg/L) Cu (mg/L) Fe (mg/L) Hg (mg/L) K (mg/L)	19 0.72 517.6 <0.1 <0.4 0.65 19.6 <0.0005 <0.002 0.077 143 0.011 0.039 0.018 0.062 0.0012 2.01	26.5 0.185 328.3 <0.1 <0.4 <0.02 97.2 <0.01 <0.002 0.072 119 <0.002 <0.02 <0.01 2.67 <0.0002 2.16	19 <0.5 ^b 422.7 0.44 0.584 0.342 385 <0.01 <0.002 0.090 196 <0.002 <0.02 <0.01 4.30 <0.0002 1.35	38 0.17 308.3 <0.1 1.32 0.024 121 <0.01 <0.002 0.05 88.6 <0.002 <0.002 <0.01 0.02 <0.0002 2.62	15 0.17 344.3 <0.1 8.72 NR 54.2 <0.0005 <0.002 0.044 108 0.004 0.025 0.012 0.043 0.0006 2.1
Mg (mg/L) Mn (mg/L) Mo (mg/L) Na (mg/L) Ni (mg/L) Pb (mg/L) Se (mg/L) Th (mg/L) U (mg/L)	72.8	27.9	33.8	24.2	25.7
	0.01	0.198	0.40	0.03	0.012
	<0.02	<0.033	<0.02	<0.02	<0.02
	15.4	11.6	9.5	16.8	9.12
	0.034	<0.02	<0.02	<0.02	<0.02
	<0.002	<0.002	0.032	0.003	<0.002
	<0.002	<0.002	<0.002	<0.002	<0.002
	<0.008	<0.002	<0.004	<0.002	0.005
	0.81	<0.002	0.005	0.033	0.283

^aNR = analysis not reported bLess than sign indicates below detection limit value

APPENDIX A ANALYTICAL RESULTS FOR MODELED GROUNDWATERS

WELL #	2046	2060	2060	2061	2094
Sample ID	3997	3696	3889	3890	3872
Sample Date	02/02/89	10/25/88	02/01/89	02/07/89	02/01/89
Round #	4	3	4	4	4
pH	7.1	7.5	7.4	7.6	7.1
Eh (mV)	441	NR ^a	477	415	75
O ₂ (mg/L)	4	3.2	2	0.7	0.4
T (^O C)	9	11	8	6	15
CI (mg/L) F (mg/L) HCO3 ⁻ (mg/L) NH4 ⁺ (mg/L) NO3 ⁻ (mg/L) P (mg/L) SO4 ⁻² (mg/L) Ag (mg/L) As (mg/L) Ca (mg/L) Cd (mg/L) Cr (mg/L) Cu (mg/L) Fe (mg/L) Hg (mg/L) K (mg/L) Mg (mg/L) Mn (mg/L) Na (mg/L) Na (mg/L)	3 0.15 355.3 <0.1b 5.98 0.39 73.5 <0.0005 <0.002 0.067 111 0.006 0.023 0.021 0.117 <0.0002 2.86 31.8 0.017 <0.02	21 0.54 265.5 <0.1 32.8 <0.02 36 <0.01 <0.002 0.039 81.8 <0.002 <0.02 <0.01 0.011 <0.0002 2.27 20.8 0.001 <0.02 10.6	22 0.48 276.6 <0.1 1.51 0.03 78.3 <0.0005 <0.002 0.054 90.6 <.02 0.03 0.018 0.161 0.001 5.58 24.3 0.01 <0.02 13.6	19.5 0.33 262.5 0.266 1.73 0.02 61.8 <0.0005 <0.002 0.044 87 0.006 0.026 0.027 0.18 <0.0002 2.77 22.6 0.016 <0.02 10.6	185 0.17 716.6 <0.1 <0.4 1.92 33 <0.0005 0.21 1.25 . 74 0.011 0.03 0.026 21.2 0.0085 1800 49.4 0.256 <0.02 109
Ni (mg/L) Pb (mg/L) Se (mg/L) Th (mg/L) U (mg/L)	0.02	<0.02	<0.02	<0.02	0.052
	0.006	<0.002	<0.002	0.004	<0.002
	0.003	<0.002	<0.002	0.002	<0.002
	<0.002	<0.007	<0.003	<0.003	<0.004
	0.309	0.171	0.25	0.292	0.0045

^aNR = analysis not reported ^bLess than sign indicates below detection limit value

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APPENDIX A ANALYTICAL RESULTS FOR MODELED GROUNDWATERS

WELL #	2095	3001	3001	3013	3013
Sample ID	3787	3783	3936	3703	3899
Sample Date	12/06/88	12/05/88	02/28/89	11/14/88	02/22/89
Round #	3	3	4	3	4
pH	7.33	8	7.1	6.3	8.4
Eh (mV)	NR ^a	NR	81	NR	139
O ₂ (mg/L)	4.1	9.5	0.7	1.9	NR
T (⁰ C)	11	9	11	13.5	7
CI (mg/L) F (mg/L) HCO3 ⁻ (mg/L) NH4 ⁺ (mg/L) NO3 ⁻ (mg/L) P (mg/L) SO4 ⁻² (mg/L) As (mg/L) As (mg/L) Ba (mg/L) Ca (mg/L) Cd (mg/L) Cr (mg/L) Cu (mg/L) Fe (mg/L) Hg (mg/L) K (mg/L)B Mg (mg/L) Mn (mg/L)	4 0.24 352.2 <0.1 77.5 0.063 17.5 <0.02 <0.002 0.05 100 <0.002 <0.02 0.014 0.032 0.0004 2.5 23.3 0.003	19.1 0.19 300.7 .131 <0.4 <0.02 176 <0.002 <0.002 <0.002 <0.002 <0.01 4.5 <0.0002 5.56 37.9 0.362	21 0.1 300.9 0.5 <0.08 0.12 67 <0.01 <0.003 0.053 100 <0.005 0.02 <0.01 2.5 <0.0002 2.3 25 0.61	60 0.113 480.5 <0.1 <0.4 <0.02 252 <0.01 <0.002 0.089 202 0.007 <0.02 <0.01 7.21 <0.0002 3.85 45.2 0.382	21 0.45 302.2 0.1 0.4 0.02 130 <0.01 <0.003 0.071 68 0.007 0.4 0.01 0.05 <0.0002 2 52 0.02
Mo (mg/L) Na (mg/L) Ni (mg/L) Pb (mg/L) Se (mg/L) Th (mg/L) U (mg/L)	<0.02	<0.02	0.01	0.041	0.02
	24.6	24.4	11	45.7	18
	<0.02	<0.02	<0.03	<0.02	<0.03
	<0.002	<0.002	<0.002	0.004	<0.002
	<0.002	<0.002	<0.005	<0.002	<0.005
	<0.004	<0.006	<0.003	<0.006	<0.003
	0.177	0.015	0.015	0.011	0.490

^aNR = analysis not reported ^bLess than sign indicates below detection limit value

APPENDIX A ANALYTICAL RESULTS FOR MODELED GROUNDWATERS

WELL #	3014	3016	3062	3069	3094
Sample ID	3672	3686	3780	3663	3874
Sample Date	11/06/88	11/04/88	10/25/88	11/07/88	02/01/89
Round #	3	3	3	3	4
pH	7.75	7.6	7.9	7.6	7.1
Eh (mV)	NR ^a	NR	NR	NR	99
O ₂ (mg/L)	6.2	5.1	6.8	3.82	0.6
T (^O C)	12	13.5	11	9.5	15
CI (mg/L) F (mg/L) HCO3 ⁻ (mg/L) NH4 ⁺ (mg/L) NO3 ⁻ (mg/L) P (mg/L) SO4 ⁻² (mg/L) Ag (mg/L) As (mg/L) Ba (mg/L) Ca (mg/L) Cd (mg/L) Cr (mg/L) Cu (mg/L) Fe (mg/L) Hg (mg/L) K (mg/L) Mg (mg/L) Mn (mg/L) Mo (mg/L)	25.8 0.16 229.4 <0.1b 7.44 <0.02 51.4 <0.01 <0.002 0.03 74.1 0.004 <0.02 <0.01 0.03 <0.0002 1.94 18.7 <0.001 <0.02	25.6 0.15 251.4 <0.1 13.5 <0.02 174 <0.01 <0.002 0.040 82.9 <0.002 <0.002 <0.01 0.10 <0.0002 2.53 21.4 0.050 <0.02	19.9 0.32 312.8 <0.1 <0.4 <0.02 29 <0.01 <0.002 0.063 92.3 <0.002 <0.002 <0.001 1 <0.0002 2.16 22.7 0.396 <0.02	24.5 0.18 261.0 0.17 2.97 0.662 92.7 <0.01 <0.002 0.050 79.6 <0.002 <0.02 <0.01 0.10 <0.0002 2.15 20.6 0.10 <0.02	140 0.13 710.6 2.4 <0.4 0.88 41.2 <0.0005 0.003 0.382 106 0.007 0.032 0.02 4.43 0.0023 1830 58.1 0.241 <0.002
Na (mg/L) Ni (mg/L) Pb (mg/L) Se (mg/L) Th (mg/L) U (mg/L)	10.9	11.3	12.9	11.4	90.1
	<0.02	<0.02	<0.02	<0.02	0.066
	0.016	0.003	<0.002	0.010	<0.002
	0.002	0.002	<0.002	0.002	<0.002
	<0.007	NR	<0.002	NR	<0.003
	0.028	0.008	0.041	0.005	0.0006

^aNR = analysis not reported ^bLess than sign indicates below detection limit value

APPENDIX A ANALYTICAL RESULTS FOR MODELED GROUNDWATERS

WELL # Sample ID Sample Date Round #	4097 3988 02/08/89 4	
pH Eh (mV) O ₂ (mg/L) T (⁰ C)	7.1 221 0.5 11	
CI (mg/L) F (mg/L) HCO3 ⁻ (mg/L) NH4 ⁺ (mg/L) NO3 ⁻ (mg/L) P (mg/L) SO4 ⁻² (mg/L) Ag (mg/L) As (mg/L) Ba (mg/L) Ca (mg/L) Cd (mg/L) Cr (mg/L) Cu (mg/L) Fe (mg/L) Hg (mg/L) Hg (mg/L) Mn (mg/L) Mn (mg/L) Na (mg/L) Ni (mg/L) Pb (mg/L) Se (mg/L) U (mg/L) U (mg/L)	25 0.16 329.7 .247 .53 0.11 66.4 <0.0005 ^a <0.002 0.055 94.7 0.006 0.024 0.01 0.743 0.0006 2.17 27.6 0.243 <0.02 15.1 <0.02 <0.002 0.003 <0.002 0.003 <0.002	

^aLess than sign indicates below detection limit value